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## Synthesis and characterization of magnetite nanoparticle coated humic acid (Fe<sub>3</sub>O<sub>4</sub>/HA)

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### Abstract

Magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) coated humic acids (HA) by a co-precipitation method using ammonium hydroxide. The HA was extracted from peat soil of Sambutan, East Kalimantan, Indonesia and then have been successfully coated onto the surface of Fe<sub>3</sub>O<sub>4</sub>. Characterization of FT-IR spectra indicate that the coating Fe<sub>3</sub>O<sub>4</sub>/HA have been bound by Fe-COOR chemical bond. The XRD measurements does not affect the crystals structure. Scanning electron microscopy revealed the magnetic particle size is almost homogenous of 10-18 nm. Both of Fe<sub>3</sub>O<sub>4</sub> and the coating Fe<sub>3</sub>O<sub>4</sub>/HA were of the cubic spinel structure and spherical-shaped morphology. The modification of HA on Fe<sub>3</sub>O<sub>4</sub> can decrease the saturation magnetization from 71.3 emu/g to 69.5 emu/g.

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*Keywords:* synthesis; characterization; magnetite; humic acids; peat soil

### 1. Introduction

Magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) have unique size, physical properties and potential applications in biomedical, biotechnology, materials sciences, engineering and environmental. The most studied materials due to their response to magnetic field, high saturation magnetization, non-toxic and biocompatible[1,2]. The magnetite nanoparticles are susceptible to air oxidation and easily aggregated in aqueous system Thus, the stabilization of magnetite is desirable [3,4.]

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The humic acids (HA) are natural macromolecular compound with multi functional group dominated by carboxyl and hydroxyl group. The functional group on HA possess different ability in binding metal ion through complex formation [5]. The Indonesian terrestrial HA were very specific in their oxygen containing principal aims of this study are to characterize the groundwater hydrochemistry in different monsoon seasons and to determine the extents of saltwater intrusion in Kapas Island aquifer based on the ionic strength of selected ions.

Coating of particle surface can effectively prevent the adhesion of colliding particles during thermal motion. Binding HA on Fe<sub>3</sub>O<sub>4</sub> influences the sorption because the adsorption of HA result polyanionic organic coating on Fe<sub>3</sub>O<sub>4</sub> and thus essentially altering the surface properties. The adsorption capacity for metal cations with complex HA and Fe<sub>3</sub>O<sub>4</sub> was reported to be larger than that with the respective HA or Fe<sub>3</sub>O<sub>4</sub> alone [6,7,8]. Recent research indicated HA has high affinity to Fe<sub>3</sub>O<sub>4</sub> nanoparticles enhanced the stability of nano dispersion by preventing their aggregation [9,10].

In this work, we developed the coating Fe<sub>3</sub>O<sub>4</sub>/HA using humic acid from peat soil of Sambutan, East Kalimantan on Fe<sub>3</sub>O<sub>4</sub> by co-precipitation methods and characterization of spectrum consist of functional groups, crystal structure, morphologys, dispersion and size distribution and magnetic properties were investigated.

## 2. Methods

### 2.1. Study site

The reagents of analytical grade i.e., FeCl<sub>3</sub>.6.H<sub>2</sub>O, FeSO<sub>4</sub>.7.H<sub>2</sub>O, NH<sub>4</sub>OH 25%, C<sub>6</sub>H<sub>5</sub>OH, HCl, HF, H<sub>2</sub>O<sub>2</sub>, NaOH, N<sub>2</sub>.

### 2.2. Extraction and purification of HA from Sambutan village, Samarinda, East Kalimantan

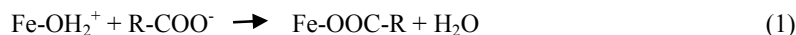
The humic acid (HA) was extracted of peat soil in 0.1 M NaOH under nitrogen atmosphere at ambient temperature with and mechanical stirring overnight. The suspension was centrifugated and then filtered and the filtrate was precipitated with 6 HCl. The precipitated was centrifugated then precipitate was purified with HCl and HF. The HA obtained were washed with distilled water and dried in vacuum.

### 2.3. Preparations and characterization of Fe<sub>3</sub>O<sub>4</sub>/HA

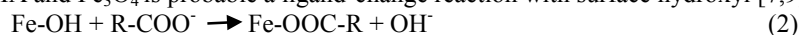
The coating Fe<sub>3</sub>O<sub>4</sub>/HA was prepared by the co-precipitation method, FeCl<sub>3</sub>.6.H<sub>2</sub>O and FeSO<sub>4</sub>.7H<sub>2</sub>O were dissolved into 25 mL water and heated to 90 °C. Then added of NH<sub>4</sub>OH 25% until pH 11 and 0.125 g of humic acids sodium salt dissolved in 12.5 mL of water were added rapidly and sequestially. The mixture was aged at 90 °C for 30 minutes and then cooled to room temperature. The black precipitate was separated from solution and washed to neutral with water. The functional group of Fe<sub>3</sub>O<sub>4</sub>/HA, Fe<sub>3</sub>O<sub>4</sub> and HA were characterized by Fourier transform spectrometer (FT-IR) 8201 PC Shimadzu. The crystal structure was analyzed by X-ray diffraction (XRD) Shimadzu using CuK $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) operated at 40kV and 30 mA.. The size and morphologies of nanoparticles were determined by Transmition electron microscopy (TEM, JEOL JEM 1400). The magnetic nanoparticles properties were measured by Vibrating sample magnetometer (VSM, Oxford).

## 3. Results and discussion

The magnetite is an amphoteric solids, which can develop charges in the protonation and deprotonation reaction of Fe-OH sites on surface. This process is controlled by the pH and ion strength in aqueous medium. At pH lower than the PZC (pH < 7.9) the surface charge is positive, electrostatic interaction between HA and Fe<sub>3</sub>O<sub>4</sub> is and dominant under acidic conditions.



At above the pH of PZC (pH > 7.9) the surface charge is negative, the coating HA on Fe<sub>3</sub>O<sub>4</sub> in alkaline condition, the dominant interaction between HA and Fe<sub>3</sub>O<sub>4</sub> is probable a ligand-change reaction with surface hydroxyl [7,9].



Identification of functional group of HA from peat soil of Sambutan village, East Kalimantan, Indonesia was presence of O-H stretching ( $3425\text{ cm}^{-1}$ ). The absorption band at  $2924\text{ cm}^{-1}$  was stretching vibration of aliphatic C-H in  $\text{CH}_2$  or/and  $\text{CH}_3$ , wavenumber  $1706\text{ cm}^{-1}$  and  $1627\text{ cm}^{-1}$  were attributed to the stretching  $\text{C}=\text{O}$  of  $\text{COOH}$  and  $\text{COO}^-$  asymmetric stretching vibrations and stretching of aromatic  $\text{C}=\text{C}$ , respectively. The FTIR spectra of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{HA}$  centered at  $563\text{ cm}^{-1}$  were attributed to the stretching vibration of Fe-O bond. Succesfully coating of  $\text{Fe}_3\text{O}_4/\text{HA}$  shows the  $\text{C}=\text{O}$  stretching at  $1404\text{ cm}^{-1}$ , indicating the carboxylate anion interacting with FeO as the  $\text{C}=\text{O}$  stretches in free carboxylate acids (Fig.1) [8,9,10].

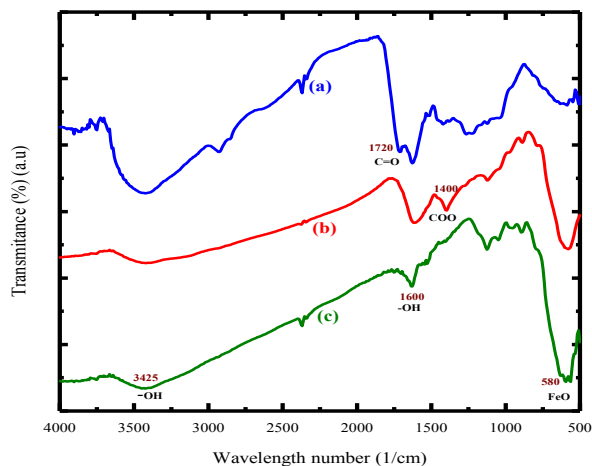


Fig 1. FTIR Spectra of humic acid (HA) from Sambutan village, Samarinda, East Kalimantan (a),  $\text{Fe}_3\text{O}_4$  (b) and  $\text{Fe}_3\text{O}_4/\text{HA}$  (c)

The XRD measurement was used to identify the crystalline structure of the product. The XRD patterns of  $\text{Fe}_3\text{O}_4/\text{HA}$  and  $\text{Fe}_3\text{O}_4$  are shown in Fig 2.

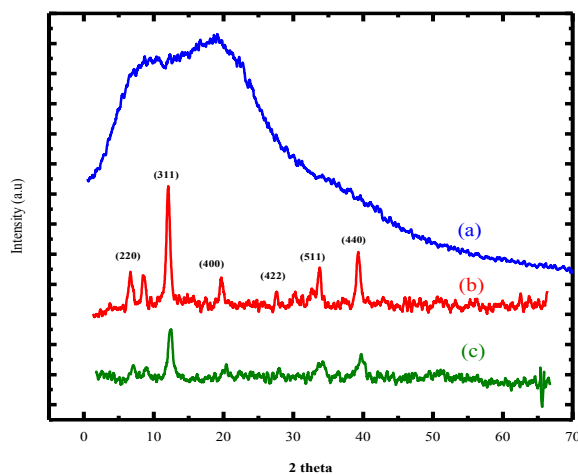


Fig 2. XRD pattern of humic acid (HA) from Sambutan village, Samarinda, East Kalimantan (a),  $\text{Fe}_3\text{O}_4$  (b) and  $\text{Fe}_3\text{O}_4/\text{HA}$  (c)

Two materials had similar diffraction peaks at  $2\theta = 30,1^\circ, 35,4^\circ, 43,1^\circ, 57,0^\circ, 62,68^\circ$  dan  $74,5^\circ$ . The XRD peaks can match well with the characteristic peaks of inverse cubic spinel structure (JCPDS 19-0629). This result indicated that the crystal structure of  $\text{Fe}_3\text{O}_4$  was not changed after modification with HA [2,11]. The average crystallite  $d$  calculated using the Debye-Scherrer equation  $d = K\lambda/(\beta\cos\theta)$  are about  $\text{Fe}_3\text{O}_4 = 13.46$  nm and  $\text{Fe}_3\text{O}_4/\text{HA} = 10.80$  nm.

The morphology and mean particles size of these samples characterized by SEM (Fig. 3). The SEM images of HA was colloid-rigid shape. The magnetite shown homogenously spherical-shape and had distribution of particles size between 10-18 nm. This result is in agreement with the result of XRD analysis. The HA modified  $\text{Fe}_3\text{O}_4$  shown coverage of HA on the surface  $\text{Fe}_3\text{O}_4$  that significantly increased in the size and also well dispersed, which indicated HA efficiently reduces their aggregation [12]. Composition of C and O at magnetite coated HA was increased and then Fe was decreased after coating  $\text{Fe}_3\text{O}_4/\text{HA}$ .

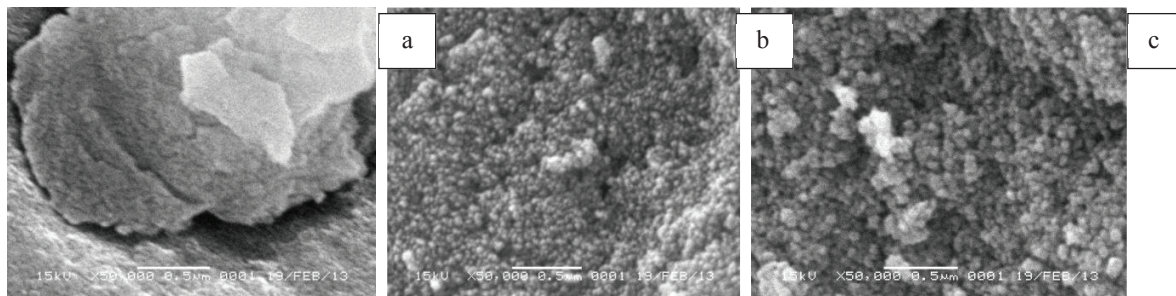


Fig. 3. SEM images of humic acids (a),  $\text{Fe}_3\text{O}_4$  (b) and humic acid coated  $\text{Fe}_3\text{O}_4$  ( $\text{Fe}_3\text{O}_4/\text{HA}$ )

No	composition of element (%mass)	HA	$\text{Fe}_3\text{O}_4$	$\text{Fe}_3\text{O}_4/\text{HA}$
1	C	63,44	2,69	5,91
2	O	33,79	8,40	10,53
3	Fe	2,77	88,91	83,57

The comparison of saturation magnetization ( $M$ ) of  $\text{Fe}_3\text{O}_4$  and after magnetite coated HA at Fig 4. The saturation magnetization of  $\text{Fe}_3\text{O}_4$  higher than magnetite coated HA, 71.3 emu/g and 69.5 emu/g. This saturation magnetization decreases evidently when  $\text{Fe}_3\text{O}_4$  were modified with HA because attribute to the surface small particle spin effect which result in the reduction of magnetic moments of magnetite.

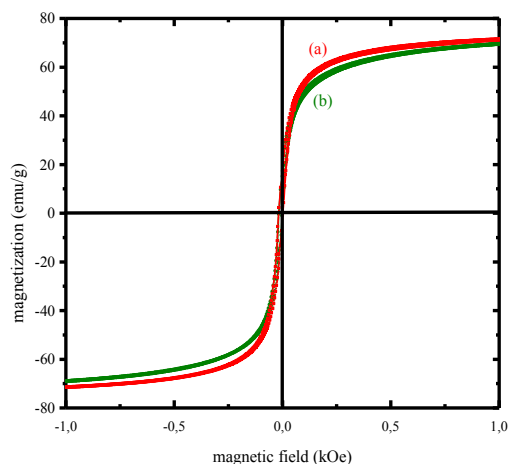


Fig 4. Magnetization curve of  $\text{Fe}_3\text{O}_4$  (a) and  $\text{Fe}_3\text{O}_4/\text{HA}$  (b)

#### 4. Conclusion

The magnetite coated HA could be success to synthezed with the FT-IR spectra reveals that HA have been successfully coated onto surface of  $\text{Fe}_3\text{O}_4$  by chemical bond. The modification HA on  $\text{Fe}_3\text{O}_4$  does not affect the crystals structure, decrease the saturation magnetization and excellent dispersion, which. indicated HA efficiently reduces their aggregation.

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#### References

1. Faraji, M., Yamini, Y and Rezaee, M., 2010, Magnetic nanoparticles : synthesis, stabilizations, functionatization, characterization and application, *J. Iran. Chem.Soc*, 7, 1-37
2. Petcharoen, K., and Sirivat, A., 2012, Synthesis and characterization of magnetic nanoparticles via the chemical co-precipitation method, *Mater. Sci.Eng.B*, 177, 421-427
3. Maity D., and Agrawal, C., 2007, Synthesis of iron oxide nanoparyicles under oxidizing environment and their stabilization in aqueous and non-aqueous media, *J. Mag.Magn.Mater.*, 308, 46-55
4. Carlos, L., Cipollone, M., Soria, D.B., Moreno, M.S., Ogilby, P.R., Einschlag, F.S.G., Martire, D.O., (2012). The Effect of Humic Acids Binding to Magnetite Nanoparticles on The Photodegradations of Reactive Oxygen Species, *Sep. Purif.Technol*, 91, 23-29
5. Stevenson, F.J.,(1994). *Humus Chemistry*, second edition, John Wiley and Sons, New York
6. Santosa, S.J., Tanaka, S., Siswanta, D., Kunarti, E.S, Sudiono, S., Rahmanto, W.H., 2007, Indonesian peat soil derived humic acids, it's characterization, immobilization and performance as metal adsorben, *Proceeding of International Conference on Chemical Sciences*, Yogyakarta
7. Tombacz, E, Horvat, M., and Illes, E., 2006, Magnetite in aqueous medium : coating its surface and surface coated with it, *Rom.Rep.Phys.*, 58, 281-286
8. Liu, J.F., Zhao, Z.S. and Hang, G.B, (2008). Coating  $\text{Fe}_3\text{O}_4$  magnetic nanoparticle with Humic Acids for High Efficient Removal of Heavy Metals in Water, *Environ.Sci. Technol*, 42, 6949-6954
9. Illes, E., and Tombacz, E., 2005, The role of variable surface charge and surface complexation in the adsorption of humic acid on magnetite, *J. Colloid Surf. A*, 203, 99-109
10. Illes, E., and Tombacz, E., 2006, The effect of humic acids adsorption on pH-dependent surfece charging ang aggr, egation of magnetic nanoparticles, *J. Colloid Surf. A*, 295, 115-123

11. Wei, Y., Han, B., Hu, X., Lin, Y., Wang, X., Deng, X., (2012). Synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and their magnetic properties, *Procedia Eng.* 27, 632-637
12. Niu, H., Zhang, D., Zhang, S., Zhang, X., Meng, Z., Cai, Y., (2011). Humic Acid coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticle as highly efficient Fenton-like catalyst for complete mineralization of sulfathiazole, *J.Hazard Mater* 190, 559-565