

.b.1.2._ARPN_journal_Engineering_Applied_Science_2016-soerja.pdf
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Submission date: 19-Jun-2023 06:47AM (UTC+0700)

Submission ID: 2118512398

File name: .b.1.2._ARPN_journal_Engineering_Applied_Science_2016-soerja.pdf (309.81K)

Word count: 2226

Character count: 11669



MODIFICATION OF MAGNETITE COATED HUMIC ACIDS ($\text{Fe}_3\text{O}_4/\text{HA}$) TO DEGRADATION OF HEAVY METAL Cu AND Cr FROM LIQUID WASTE ON PLYWOOD INDUSTRIES

Soerja Koesnarpadi and Daniel

Department of Chemistry, Mathematics and Natural Sciences, Mulawarman University, Samarinda, Indonesia

E-Mail: soerja.koes@gmail.com

ABSTRACT

Modification adsorbent of magnetite (Fe_3O_4) coated humic acids (HA) by a co-precipitation method using ammonium hydroxide have been successfully synthesized. The characterization of FT-IR spectra indicate that the coating $\text{Fe}_3\text{O}_4/\text{HA}$ have been bound by Fe-COO-R and the XRD patterns does not have effect of the crystals structure. It's applications to degrade of heavy metal Cu and Cr from liquid waste on plywood industries. Degradation of Cu on $\text{Fe}_3\text{O}_4/\text{HA}$ and Fe_3O_4 i.e up 70-90% and then for Cr on $\text{Fe}_3\text{O}_4/\text{HA}$ and Fe_3O_4 i.e 10-40% only. The performance adsorbent of $\text{Fe}_3\text{O}_4/\text{HA}$ more effectively than Fe_3O_4 for degradation of heavy metal Cu and Cr.

Keywords: modification, magnetite, humic acids, degradation, cu and cr, liquid waste.

INTRODUCTION

The coating of surface materials was protective of adsorbent material that serves to make the material properties more attractive, easier to use and can be used for a long time [1]. Magnetite (Fe_3O_4) and humic acid (HA) were a good adsorbent to adsorb of heavy metals. The properties of Fe_3O_4 have unique and characteristic size nanoparticle, high saturation magnetization but susceptible to air oxidation and easily aggregated in aqueous. The HA was macromolecule compound with multifunctional groups but existence on acidic condition only [2]. Therefore, modification of coating HA on Fe_3O_4 particle surface enhanced the stability of nanodispersion by preventing their aggregation by electrostatic, steric or combined stabilization layer, increasing the absorption capacity and did not clot in a wide pH range [3, 4].

The heavy metals of Cu and Cr were categorized very toxic industrial waste. The presence of heavy metals in the environment could be contamination of the waters [5]. According to Government Regulation No. 82/2001 that the heavy metals in environment for Cu i.e 0.2 mg/L and Cr i.e 0.01 mg/L. The processing of plywood industries has liquid waste of phenol but the presence of heavy metals also need to be monitored.

For previous research, the adsorbents of $\text{Fe}_3\text{O}_4/\text{HA}$ were used to adsorb of heavy metals Hg, Pb, Cu and Cr from water [6], sulfathiazole [7], benzene [4] and rhodamine B [8]. And then, functional groups of humic acid are dominant depending on climate zone region so that the COOH and OH groups on each different region [9]. In this research will be modification of Fe_3O_4 coated HA by co-precipitation method in which the HA was extracted of peat soil from Sambutan village, East Kalimantan. And then to determine the performance of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$ for degradation of heavy metal Cu and Cr from liquid waste on plywood industries.

LITERATURE REVIEW

Magnetite (Fe_3O_4)

Magnetite (Fe_3O_4) is ferromagnetic mineral containing Fe(II) and Fe(III) and has crystal structure inverse spinel with a unit cell consisting of 32 oxygen in face-centered cubic structure.

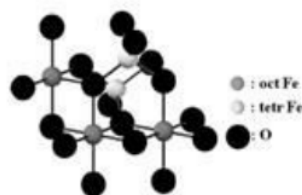


Figure-1. Crystal structure of Fe_3O_4 [10].

The properties of Fe_3O_4 have unique size nanoparticle, high saturation magnetization, uniform surface morphology but susceptible to air oxidation and easily aggregated in aqueous [2].

Humic acids (HA)

The HA is macromolecule compound with complex functional groups such as carboxylic groups, phenolic or hydroxyl but existence on acidic condition only [11]. According Klavin and Eglite [12], Hypothetic structure of HA to illustrate with reactive of functional groups such as hydroxyl, alcoholic, phenolic, carboxyl and amide to perform reactions of immobilization.

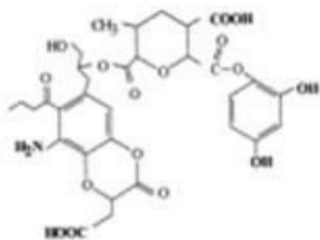


Figure-2. Hypothetic structure of HA [12].

The coating of Fe₃O₄/HA

The binding HA on Fe₃O₄ was essentially altering the surface properties, stability of colloidal magnetite [13], increasing the particle size, pressing strength and stability of the magnetic properties of penetration [14] and effectively preventing their aggregation [3].

The magnetite coated HA could be alkaline conditions (pH > 7.9), at above the pH of PZC the surface charge is negative, the dominant interaction between HA and Fe₃O₄ is probable a ligand-change reaction with surface hydroxyl to produce Fe-OOC-R [15]



The mechanism of magnetite was stabilized by HA was a cyclical nanocontainer [16].

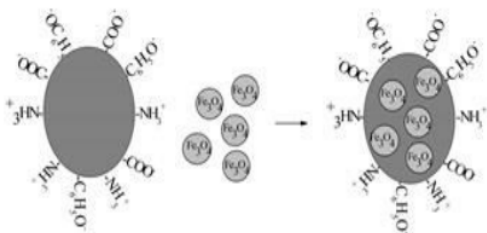


Figure-3. Mechanism of stability magnetite on HA [16].

The adsorption capacity of metal cations with Fe₃O₄/HA was reported to be larger than that with the respective HA or Fe₃O₄ alone. Liu *et al* [8] conducted that Fe₃O₄ coated HA stable in neutral acid-base aqueous solution at 0.1 M HCl to 2 M NaOH and then degradation of heavy metals by Fe₃O₄/HA was for Hg (II) and Pb (II) to 99% while for Cu (II) and Cd (II) to 95%.

Plywood industry: The existence and potential of waste

The Indonesian plywood industries developed from 1990 and culminating in 1997 and production of plywood reached 10.270 million m³. However, beginning in 2000, production of plywood declined to 4.611 million m³. This was due to the raw material begin to decreases [17]. The East Kalimantan forest still has potential in the production of processed plywood to 347,347.13 m³ in

2013 [18] so there are still some plywood industries in East Kalimantan which persist in producing plywood. The plywood industry has the potential to produce liquid waste and according to Minister of the Environment No.5/2014 that potentially liquid waste were BOD₅, COD, TSS, phenol, ammonia and pH. The phenols of very toxic and the greatest. While the presence of heavy metals also needs to be monitored due to the impact of heavy metals including dangerous for living beings.

MATERIALS AND METHODS

Materials

All reagents in analytical grade i.e., FeCl₃.6.H₂O, FeSO₄.7.H₂O, NH₄OH 25%, Standard of Cu and Cr, Nitrogen gas and Aquabidest. The Humic acid (HA) was extracted from peat soil in Sambutan village, Samarinda, East Kalimantan, Indonesia.

METHODS

Modification of Fe₃O₄ coated HA

The coating of Fe₃O₄/HA was prepared by the coprecipitation method. FeCl₃.6.H₂O : FeSO₄.7H₂O (3:2) were dissolved into 25 mL water and heated to 90 °C. Added gradually of NH₄OH 25% until pH 11 for 30 minutes by magnetic stirrer to form a black powder in the solution. Then 0.125g of HA sodium salt dissolved quickly in 12.5 mL of water were added rapidly and sequentially. The mixture was aged at 90 °C for 30 minutes and then cooled to room temperature. The black precipitate was separated from solution by filtering and washed to neutral with water. The characterization of precipitate by FTIR spectrometer and XRD.

Sampling of liquid waste on plywood industries

The sample of liquid waste from Mahakam river and plywood industries such as SLJ, KLM and TMR. Then analysis preliminary of Cu and Cr on plywood industries by Atomic Absorption Spectrophotometer.

Performance of Fe₃O₄/HA and Fe₃O₄ for degradation Cu and Cr

The sample of liquid waste was added standard of Cu and Cr and then 0.3 g Fe₃O₄/HA and Fe₃O₄. The performance of Fe₃O₄/HA and Fe₃O₄ using batch method system were for 0, 3 and 6 hours. The mixture was filtered and the filtrate was determined by Atomic Absorption Spectrophotometer.

RESULT AND DISCUSSION

The synthesis of Fe₃O₄ and coating of Fe₃O₄/HA were prepared by the co-precipitation method and then adsorbent was characterized by FT-IR spectrometer and XRD.

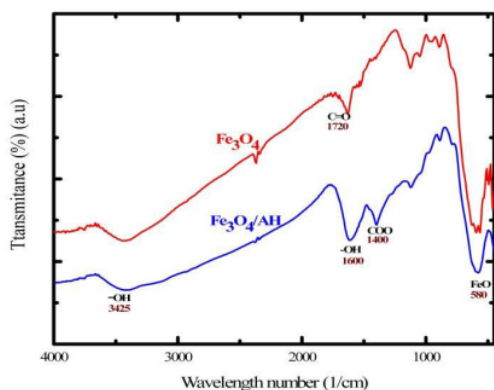


Figure-4. FT-IR Spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$

The FT-IR spectra Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{AH}$ obtained at 563 cm^{-1} were attributed to the stretching vibration of Fe-O bond and OH at 3425 cm^{-1} . Coating of $\text{Fe}_3\text{O}_4/\text{HA}$ successfully shows the C=O stretching at 1400 cm^{-1} and loses 1700 cm^{-1} at Fe_3O_4 . This indicate of carboxylate anion interacting with FeO as the C=O stretches in free carboxylate acids [4]

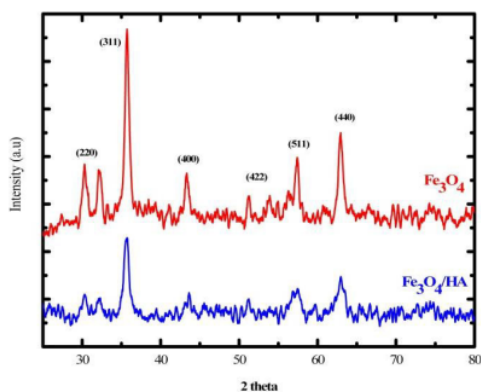


Figure-5. XRD pattern of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$.

The XRD patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$ 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 measurement was used to identify the crystalline structure of the product. The XRD peaks can match well with the characteristic peaks of inverse cubic spinel structure (JCPDS 19-0629). This result indicates that the crystal structure of Fe_3O_4 was not changed after modification with HA.

Performance of $\text{Fe}_3\text{O}_4/\text{HA}$ and Fe_3O_4 for degradation Cu

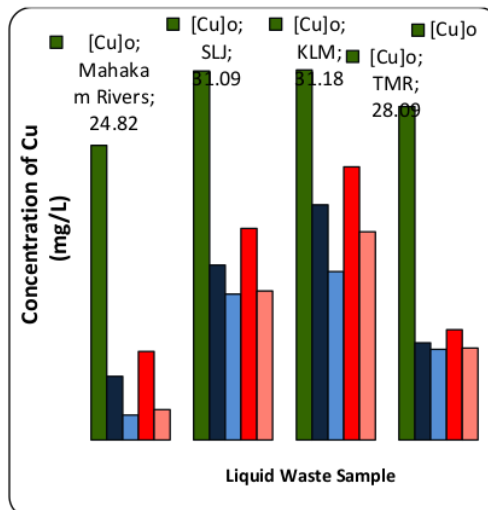


Figure-6. Histogram of degradation Cu by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$ for 0, 3 and 6 hours.

Degradation of Cu on Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$ for 3 and 6 hours i.e up to 70- 90%. This is due to that the plywood waste that mostly in form of anions and rarely in the form of cations, so that the Cu cation on liquid waste on plywood industries will be maximum of degraded on the adsorbent.

Performance of $\text{Fe}_3\text{O}_4/\text{HA}$ and Fe_3O_4 for degradation Cr

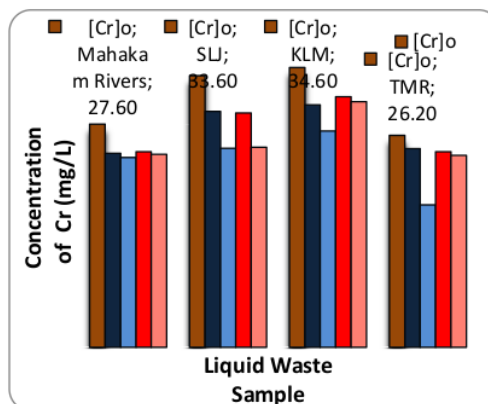


Figure-7. Histogram of degradation Cr by Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$ for 0, 3 and 6 hours.

The degradation of Cr on Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$ for 3 and 6 hours were relatively small i.e only 10-40%.



This caused that the plywood waste pollutants mostly anions, such as phenol, chlorophenol or nitrophenol etc, while Cr in water in the form of anions. This is due to competition of degrade Cr and phenol waste. In general, degradation of Cu and Cr using $\text{Fe}_3\text{O}_4/\text{HA}$ more effective than using Fe_3O_4 .

CONCLUSIONS

Modification of Fe_3O_4 coated Humic acid ($\text{Fe}_3\text{O}_4/\text{HA}$) could be successfully synthesized and effective to degradation of heavy metal Cu and Cr. Degradation of Cu on $\text{Fe}_3\text{O}_4/\text{HA}$ and Fe_3O_4 were greater than degradation of Cr. Degradation of Cu and Cr using $\text{Fe}_3\text{O}_4/\text{HA}$ more effectively than using Fe_3O_4 .

ACKNOWLEDGEMENTS

We gratefully acknowledge the Ministry of Higher Education, Republic of Indonesia for providing financial research of HIBAH BERSAING step 2.

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