Effect of Solution pH to Indigosol Blue Adsorption on Humic Acid Isolated from Kalimantan Peat Oil

Gita Citra Santi^{*}, Maya Rahmayanti^{**}

Chemistry Department, Faculty of Science and Technology, UIN Sunan Kalijaga Jl. Marsda Adisucipto No. 1 Yogyakarta 55281, Indonesia. Telp. (0274) 558254. Fax. (0274) 586117 Email: gitaci57@gmail.com^{*}, m.rahmayanti@ymail.com^{**}

Abstract. There has been study on the isolated of humic acid and its interaction with *indigosol blue*. The objectives of study were to isolate humic acid from Kalimantan peat soil and to study pH optimation *indigosol blue* on humic acid. Isolated of humic acid using alkali extraction method with NaOH as solvent and precipitated with HCl. Humic acid was characterized using FTIR spectroscopy to determine functional group. Based on the result FTIR characterization, adsorption of humic acid was found in the wave number 3140,15 cm⁻¹ which show the vibration of -OH, 2924,09 cm⁻¹ show vibration of aliphatic -CH, 1705 cm⁻¹ show vibration -C = O of COOH, 1627,92 cm⁻¹ show vibration of C=C aromatic and 1226,73 cm⁻¹ indicate of -OH and CO from -COOH. Based on the result of study, pH optimation of *indigosol blue* at pH 5.

Keywords: Adsorption, Dyestuff, Humic acid, Indigosol blue, Peat soil

INTRODUCTION

Batik industry began to grow rapidly starting since UNESCO set batik as a world cultural heritage on October 2, 2009. This is potential that must be improved. The benefits of it was to improve the economy and reduce unemployment, while maintaining the sustainability of batik as a cultural symbol in Indonesia. On the side of usefulness, there was a serious problem, namely liquid waste. In these various processes, waste that was highly damaging to the environment was the coloring process waste because it involves dyes that contain various organic compounds. Dyestuffs are difficult to degrade and difficult to dissolve in water.

Indigosol blue was one of the most soluble and brightly colored dyestuffs. *Indigosol blue* is often used by batik industry as one of materials used for the dyeing process to produce colors on batik cloth. The problem was that dyeing dense dyes and containing high concentrations of chemicals directly discharged into the environment without first treatment will pollute the environment.

Waste color treatment methods are coagulation and flocculation, ozonation, electro-chemistry, decolorization and adsorption [1], oxidation and photocatalysis [2]. The ozonation method has a disadvantage because it requires high costs and was difficult to implement in the community [4]. The adsorption method has been used to remove dyes in the waters and can turn into non-hazardous compounds. Adsorption usually occurs on the surface of solids which are rich in functional groups -OH, -NH, -SH and -COOH [5]. One of the potential adsorbents to reduce and eliminate dyes was humic acid contained in the soil [6], [7], [8]. Humic acid has an abundance of –COOH and -OH groups which can reduce the concentration of dyes in liquid waste. Dyestuffs that are often used in the batik industry one of them was *indigosol blue*.

MATERIALS AND METHODS

The chemicals used were NaOH, NaCl, HCl, HF, humic acid, (Ba(OH)2) and Ca(CH3COO)2 solution. The equipment used included whatman paper, pH meter, shaker, FTIR, Spectrophotometer UV-VIS and Scanning Electron Microscopy (SEM).

This method of isolating peat soils refers to method suggested by International Humic Substances Society (IHSS), which was alkaline extraction. Dissolved with NaOH and precipitated with HCL. Purification by adding 1:1 HCl-HF. Determination of total acidity and carboxylic groups of humic acid using potentiometric titration method was carried out. Determination of optimum pH was carried out with variations in pH 4, 5, 6, 7 and 8.

RESULTS AND DISCUSSIONS

Humic acid in this study was isolated from Kalimantan peat soil. This method of isolating peat soils refers to methods suggested by the International Humic Substances Society (IHSS), which form alkaline extraction. Humic acid dissolves in NaOH for Nahumic salts, easily dissolves in air. Humic acid was precipitated with 0.1 M HCl to pH 1 Since humic acid does not dissolve in acids, the acidity was higher, the more deposits are obtained. The precipitation process was carried out by adding 0.1 M HCl, the humic acid obtained was purified with humic acid with 0.1 M: HF 0.3 M HCl solution (1:1) and carried out twice to remove inorganic compounds, especially silica.

 Table 1. Comparison of interpretation of wavenumber IR spectra of Stevenson humic acid and this study.

Humic uptake (cm ⁻¹)			Vibration type
	Stevenson (1994)	This Research	_
	3400	3410,15	Stretching vibration -OH
	2940-2900	2924,09	Stretching vibration -CH alifatik
	1725-1720	1705,07	Stretching vibration -C=O from COOH
	1610	1627,92	Stretching vibration C=C aromatic, helping asymmetry k -C=O in- COO
	1250	1226,73	-OH & C-O from - COOH

According to Stevenson [8], humic acid has major functional groups such as -OH phenolate, -OH carboxylate and -COOH. Widened and strong absorption at a wave number of 3410 cm⁻¹ in humic acid which shows a stretched -OH vibration and indicates the presence of hydrogen bonds. The peak at wave number 2924.09 cm⁻¹ in humic acid shows aliphatic -CH stretching vibration. The appearance of the absorption peak at wave number 1705.07 cm⁻¹ shows the stretch vibration of -C = O from COOH and ketones. Peak at wave number 1627.92 cm⁻¹ was aromatic C = C absorption and asymmetric stretching vibration C = O. The peak at wave number 1226.73 cm⁻ ¹ was the stretching vibration of C-O. IR spectra of humic acid as a result of this study are in accordance with Stevenson [8] which was known that humic acid has absorption at wave numbers 3400-3300 cm⁻¹ of H bonds from OH compounds, 2940-2900 cm⁻¹ CH aliphatic, 1725-1720 cm^{-1} bond C = O from COOH and ketone compounds. 1610 cm⁻¹ C = C aromatic or H bonds from C = O ketones and 1250 cm 1 CO and OH from COOH.



Figure 1. Results of AH characterization using SEM.

In (Figure 1.) the morphological shape of adsorbent of humic acid from the result of isolation has an uneven texture, almost the entire surface has a cavity. The distance between particles looks tight and the cavity was not deep enough so the surface texture looks smooth. Nonetheless, the cavity on surface of humic acid produced by isolation allows for an absorption to occur, where the solution will meet surface of the humic acid from insulation and fill the empty cavity so there was an interaction between humic acid adsorbent and *indigosol blue* solution.

One factor that affects adsorption was pH. pH variation was carried out to determine the optimum pH conditions of the adsorption of humic acid to the adsorption of *indigosol blue* dyestuff. pH conditions result in changes charge distribution on adsorbent of humic acid and *indigosol blue* as a result of protonation and deprotonation reactions of functional groups. In (Figure 2.) it was known that adsorption at an acidic pH was greater than the alkaline pH because the adsorbent will dissolve at an alkaline pH.



Figure 2. Graph of the relationship between *indigosol blue* dyes adsorbed (%) vs. pH.

In this study the pH variation starts at pH 4 because the acidic pH <4 structure of the *indigosol blue* solution will be damaged due to breakdown of the active group from indigosol blue dyestuff. In addition, at low pH (<3) humic acid tends to aggregate due to the formation of strong hydrogen bonds. It can be seen that at acidic conditions, humic acid can adsorb indigosol blue well and optimally at pH 5 with adsorption percentage of 18.6%. That was, the adsorbent of humic acid was able to adsorb the solution of *indigosol blue* until its concentration was reduced by 18.6% from its initial concentration before adsorption. In this condition, deprotonation will occur and then when the adsorbent of humic acid was added to dye solution, the surface of humic acid will undergo protonation first followed by electrostatic interactions which cause transfer of dyes in the solution to the protonated humic acid surface. Under low pH conditions there was neutralization of the negative charge on the surface of humic acid which

increases protonation and results in increased adsorption. The adsorption mechanism of *indigosol blue* on humic acid was caused by hydrogen bonds through the electrostatic interaction of H atoms from humic acid binding to O atoms.

CONCLUSIONS

Humic acid was isolated using an alkali extraction method. Characterization results with FTIR showed absorption bands at wave numbers 3140.15 cm^{-1} , 2924.09 cm⁻¹, 2337.72 cm⁻¹ and 1705 cm⁻¹. The adsorption process has an optimum pH of 5.

ACKNNOWLEDGEMENTS

Thank to the supervisor who always directs and motivates the writer.

REFERENCES

- Chen, R.P., Yin, L.Z., Lian, F.Z., Xiao, Y.W., Jian, Q.C., Ai, J.M. dan Wi, M.J. 2015. Lead (II) and Methylene Blue Removal Using a Fully Biodegradable Hydrogel Based on Starch Immobilized Humic Acid. *Chemical Engineering Journal*
- Hashemian, S., Sadeghi, B. dan Mangeli, M. 2014. Hydrotermal Synthesis of Nano Cavities of Al-MCF for Adsorption of Indigo Carmine from Aqueous Solution. *Journal of Industrial and Engineering Chemistry*.
- Lesbani, A., Miksusanti dan Setiawati, Y. 2002. Studi Interaksi Zat Warna Tekstil Auramin dengan Asam Humat Dari Tanah Gambut. *Jurnal Penelitian Sains*. ISSN: 1410-7058
- Matis K. A. 1980. Treatment of industrial liquid wastes by electrofloatation. *Water Pollution Control*
- Mohadi, Risfidian., Nurlwasa H., Sri Juari S., dan Narsito. 2008. Karakterisasi Asam Humat dari Gambut Indralaya, Ogan Ilir Sumatera Selatan. *Jurnal Penenelitan Sains*. 411-420
- Ramesh, T.N., Kirana, D.V., Ashmini,A. dan Manasa. T.R. Calcium Hydroxide as Low Cost Adsorbent for The Effective Removal of Indigo Carmine Dye in Water. *Journal of Saudi Chemical Society*. 2017. 21, 165-171.
- Stumm, W dan Morgan, J.J.1996. Aquatic Chemistry 3th. New York: John Wiley & Sons
- Stevenson, F.J.1994. Humus Chemistry: Genesis, Composition, Reactions. New York: John Wiley & Sons
- V. Prigione, G.C. Varese, L. Casieri dan V.F. Marchisio. Biosorption of Simulated Dyed Effluents by Inactivated Fungal Biomasses. *Bioresource Technology*. 2008. 99, 3559-3567.
- Waksman, S. A. 1952. Soil Microbiology. New Work: John Willey and Sons.

THIS PAGE INTENTIONALLY LEFT BLANK