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Effect Contact Time Adsorption of Naphtol Dye Using Humic Acid Adsorbent Result of Peat Isolation from Kalimantan

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Abstract. Adsorption of naphtol dye was carried out by using humic acid adsorbent from the isolation of Kalimantan peat. This study aims to determine the effect of the adsorption contact time on humic acid naphtol dyes from Kalimantan peat isolation. The purified humic acid isolation was characterized using Fourier Transform Infra-Red (FTIR), Scanning Electron Microscopy (SEM), Optical Microscopy, total acidity measurement, and measurement of -COOH (carboxylate) and -phenol OH groups. The characterized humic acid was then used as an adsorbent to adsorb the naphthol dye solution. The adsorption process was measured using a UV-Vis spectrophotometer to determine the concentration of adsorbed naphthol dye. The adsorption study of the research results showed that the optimum adsorption time of naphthol dye to humic acid was 45 minutes, this was because almost all naphtol dyes were adsorbed on humic acid.

Keywords: Adsorption, humic acid, naphthol dyes, isolation

INTRODUCTION

Indonesia is a developing country which is currently carrying out development in the industrial field. One of the fast growing industrial developments is the batik textile industry. Batik is one of Indonesia's distinctive craftsmanship. Cities that make batik as a mainstay commodity include Pekalongan, Surakarta and Yogyakarta. As we already know that the batik industry has been growing and developing since decades ago.

Batik industry is now demanded to continue to improve and improve its work standards. Small and medium batik industries are able to do and implement it, so that it can indirectly cause problems for the environment around the batik industry. Environmental problems related to textile industry activities are mostly caused by the use of organic and inorganic dyes which are difficult to dissolve in water. Some of these organic compounds are difficult to decipher, and are carcinogens. Water discoloration due to batik dye waste is still a big problem for the environment. This is because the dye is difficult to be decomposed naturally by the receiving water body.

Synthesis coloring substances (chemicals) which are disposed of carelessly without processing will cause environmental pollution. The liquid waste can cause damage to the river ecosystem so that the fish and living things in the river die. The river water also cannot be used anymore, especially if the water is polluted until it permeates and pollutes well water. Sunu (2001) states that almost all chemical dyes are toxic and if they enter the human body will stimulate cancer growth.

Disposing of colored wastewater as done by the batik industry can poison the aquatic biota in these waters. The intense color will prevent sunlight from penetrating into the body of water. This can affect the process of photosynthesis in water which results in the lack of oxygen produced in the process of photosynthesis (Setyaningsih, 2007).

The dyes most widely used by the batik industry in the city of Yogyakarta are naphtol and indigol dyes. Naphtol colorant is a compound that does not dissolve in water consists of two basic components, namely the AS naphtol group (Anilid Acid) and the color generating component, namely the diazonium group or commonly called salt, if it is combined into a colored compound if it has been dissolved (Laksono, 2012).

Adsorption is one method developed to remove pollutants (Rachmawati, 2016). The adsorption method can reduce the levels of metals in liquid waste by absorbing these metals into the surface of the adsorbent (Putra et al., 2014). Adsorption methods are generally based on the interaction of functional groups such as -OH, -NH, -SH and -COOH (Rahmawati and Sri, 2012).

In principle, dyes can interact with components from the soil or sediment, especially minerals and refractory organic materials. This level of interaction is a key factor in controlling the mobility of dyes found in the environment. According to Benerjee et al., (1973) and Ohga et al., (1990) said that binding of dyes and refractory organic materials that can occur in the environment is very limited, so research is needed on this matter. Refractory organic material in aqueous media is represented by humic substances, such as humic acid and fulvic acid (Sparks, 2003). The term humic compound was first coined by Berzelius in 1830. Humic compound is a high molecular weight macromolecular compound as a result of decomposition of plant organic matter and plays an important role in influencing soil properties and chemical species in soils and waters. The chemical structure of humic acid cannot be described as a single form because it is a complex mixture of phenol polyelectrolytes and carbohydrates that vary from one molecule to another (Hayes and Himes, 1986).

Humic compounds are found in coal and peat soils. Peat soil is the result of decay of organic matter in conditions of lack of oxygen. Based on its solubility according to Stevenson (1982) in a variety of acidity solutions, humic

compounds can be distinguished from several fractions, namely: (1) Humic acid, a fraction of humic compounds that are not soluble in water with a pH below 2; (2) Fulvic acid fraction is soluble in water with various conditions, both acids and bases; (3) Humin, is a fraction of humic compounds that are insoluble in all water conditions, both acidic and basic.

Fuch, a German scientist, has proposed the humic acid structure shown in Figure 1. The structure is the result of deduction from various studies on the humic acid structure produced from coal, which consists of aromatic rings containing the -COOH and -OH groups (Stevenson, 1994).

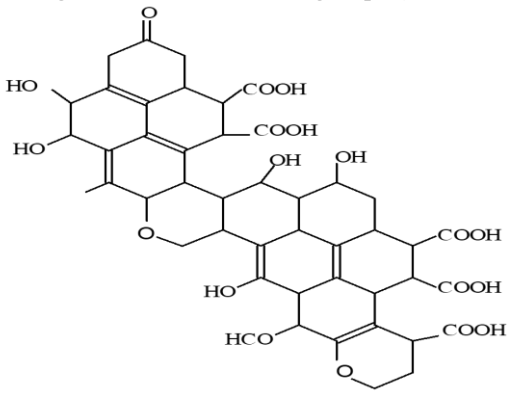

Figure 1. Hypothetical structure of humic acid according to Fuch (Stevenson, 1994).

The main characteristic of humic acid as part of the organic fraction of peat soil is its ability to adsorb organic and inorganic materials. The ability of humic compounds to interact with metal cations is caused by most functional groups of humic acid containing oxygen atoms such as -COOH, -OH phenolics, -OH enolates, -OH alcoholates and -C = O. The existence of the -COOH and -OH functional groups allows humic acid to be used as an adsorbent (Rahmawati and Sri, 2012).

Dyes are a combination of unsaturated organic substances with chromophores as binding colors with fibers. Unsaturated organic substances are a type of aromatic compounds, namely aromatic hydrocarbons and their derivatives, phenols and their derivatives and nitrogen-containing hydrocarbons (Manurung, 2004).

Naphtol dyes are a type of synthetic dyes commonly used in paper dyes, hair, fabrics and others. Naphtol dyes are included in the type of azo dyes which have two basic components, namely anylic acid and the diazonium salt color generator (Riyanto, 1995).

Dyes based on their structure can be divided into dyes nitroso, nitro, stilbene, diphenyl methane, acridin, kinolin, indigoida, aminokinon, anin and indofenol. If based on the nature of dyes can be divided into acids, bases, disperse, direct and others (Al-Kdasi, 2004). Dyes that are often used in the batik industry include remazol black, golden and yellow, methylene blue, methylene orange, naphtol, indigosol and others.

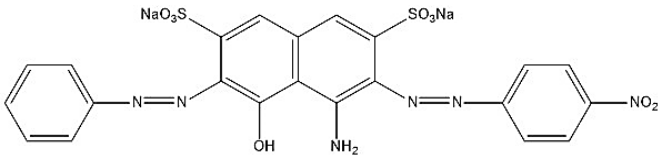

Figure 2. Chemical structure of naphtol dyes.

MATERIALS AND METHODS

The chemicals used were humic acid, naphtol dyes solution and aquadest. The equipment used included whatman paper, pH meter, shaker, and Spectrophotometer UV-VIS.

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 the optimum contact time was carried out by varying the contact time for 5, 10, 15, 30, 45 and 60 minutes at pH 2.

1. **Determination of maximum wavelength and manufacture of a standard curve for naphtol AS dye solution**

Making a standard curve is done by making a solution of 100 ppm concentration of naphtol dyes by weighing AS naphtol dyes, blue b and acoustic diazo salts as much as 0.025 g, 0.075 g and 0.0125 g, respectively. Furthermore, the acoustics are dissolved in distilled water and heated. Hot acoustic solution is used to dissolve AS naphtol, while blue b salt is dissolved in 50mL distilled water.

Next, the US naphtol solution and blue b salt were added to a 250 mL volumetric flask and added distilled water to the boundary markers and shaken until homogeneous. The 100 ppm parent solution is further diluted to 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 ppm.

The maximum wavelength is determined by measuring the solution of US naphtol dyes in the wavelength range of 400-800 nm using a UV-Vis spectrophotometer. The wavelength that has the greatest absorbance value measured is the maximum wavelength of the naphtol dye. Furthermore, the maximum wavelength is used to measure the solution of naphtol dyes with each concentration of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 ppm. Then the measurement results are plotted in the relationship curve between concentration and absorbance and include the regression value of the curve. The composition of the standard solutions used can be seen in Table 1.

Table 1. The composition of the volume of making a standard solution of naphtol dyes.

Main solution (100 ppm) taken (mL)	Final volume (mL)	Concentration (ppm)
2,5	50	5
5	50	10
7,5	50	15
10	50	20
12,5	50	25
15	50	30
17,5	50	35
20	50	40
22,5	50	45
	50	50

2. Analysis of Effect of Contact Time Adsorption Naphtol Dyes

The humic acid that has been obtained is weighed as much as 10 mg, put in a 100 mL Erlenmeyer and added with a 10 mL naphthol dye solution with the same initial concentration of 20 ppm and variations in contact time for 5, 30, 45 and 60 minutes at pH 2. Then the mixture is shaken for the variation of the contact time, then filtered with filter paper. Then analyzed by UV-Vis spectrophotometer with a predetermined wavelength of naphthol.

RESULTS AND DISCUSSION

1. Determination of Naphtol Dyes Standard Curves

The results of the measurement of the maximum wavelength of napthol dye solution using a UV-Vis spectrophotometer in this study were at 585 nm.

Naphtol dyes are substances that do not dissolve in water, so to dissolve it requires an auxiliary substance namely acoustic soda (NaOH). Based on this, the naphtol dyes are called anion dyes. The chromophore groups found in anion dyes include -N = N-, SO_3-, O- and -OH. Chromophores are groups that cause molecules to become colored. The chromophore groups in naphtol dyes have nonbonding free electron pairs, resulting in excitation with low excitation energy. This causes the naphtol dyes to have wavelengths in the visible area.

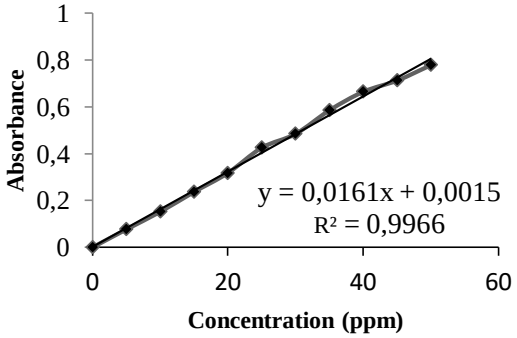

Figure 4. Standard curve for napthol dyes.

2. Effect of Contact Time Adsorption of Naphtol Dyes

This research was carried out with adsorption with humic acid as adsorbent and naphtol as an adsorbate. In the naphthol dye solution with the same initial concentration of 20 ppm and variations in contact time for 5, 30, 45 and 60 minutes at pH 2. The observations on the effect of contact time on the adsorption between humic acid and naphthol dye solutions are as follows:

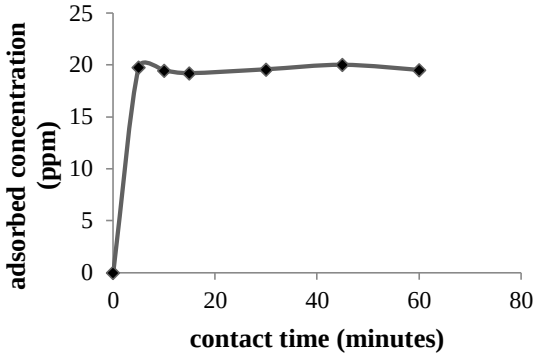

Figure 5. The curve of the influence of contact time on adsorption of naphtol dye solution

The results of this study are shown in Figure 5. that before the contact time, the concentration of the dye solution naphtol was 20.53 ppm. Then in the first 5 minutes the concentration of the naphtol dye solution that was adsorbed had a significant change, this indicated that in the first 5 minutes the adsorption process had gone very well so that the concentration of naphtol dye solution adsorbed on humic acid was quite a lot. In the following minutes, the concentration of naphtol dye adsorbed on humic acid did not show a significant change because in the first 5 minutes almost all active sites on humic acid had interacted with naphtol dye. In the adsorption process the next minutes take place gradually until the optimum time is obtained. The optimum time in this study was 45 minutes, this was because almost all naphtol dyes were adsorbed on humic acid. From the research data, the adsorption contact time can be continued with the adsorption kinetics. Adsorption kinetics aims to study adsorption related to reaction rates. Humic acid adsorption kinetics can be studied by interacting between humic acid and naphtol dye solution with time variations. The adsorption equilibrium is reached when the addition of contact time will not increase the concentration of naphtol dye solution adsorbed on humic acid as an absorbent.

CONCLUSION

Based on the research results, it can be concluded that the humic acid from the isolation of Kalimantan peat soil can absorb the optimum naphthol dye solution in contact time at 45 minutes.

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