ADSORPTION RATE CONSTANTS OF EOSIN IN HUMIN

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ABSTRACT

Eosin is one of the dyes commonly used in the industry and has the potential to cause pollution of the water environment. The Eosin pollution treatment methods used in this study was the adsorption method using humin fraction obtained from the peat land comes from Kalimantan. From the research data showed that the adsorption of eosin in humin result of washing with HCl / HF optimum at pH 4 and a contact time of 60 minutes with the adsorption-order rate was 8.4 x 10^{-3} min^{-1}.

Key Words : adsorption, eosin, humic, peat

Introduction

The development of industry in Indonesia has grown rapidly. A wide range of industries established to meet the needs of the community in various fields. One kind of industry that have been developing is industry that uses dye to produce products such as cellulose fiber dyeing, silk, wool, nylon and leather in textile industry (Razae, et al, 2008) then it can cause side effects such as an increase the quantity of waste substances color. Increase of the quantity from waste substances color is needs to be watch because the release of dye into the environment such as rivers (Rahmawati, 2011), the lake and the other will cause harmful pollution and become a source of nuisance aquatic life that require serious treatment efforts. From many existing pollutants that have been presented, eosin dye was quite dangerous to human health (Hamdaoui and Chiha, 2006) which was often used in industries other than methylene blue (Ansar, 2014).

Many kinds of research have been made to solve this problem like used activated carbon for adsorb the dye (lawakka, 2005), chitosan (Mahatmanti and Sumarni, 2003; Tanasale, 2012), Chitosan-
Bentonite (Muna, 2014), Electrochemical (marlena, 2012), a combination of activated carbon method and photo catalysis (Riyani and Setyaningtyasnamun, 2011) but the method has not been able to provide optimal results. It was necessary to find another method that could solve the problem of pollution of the dye to the water environment without having to incur huge costs and with used materials that available in nature. One method that used to adsorb dye organic waste particular was used humin which is one of the fractions of humic compounds.

The existence of humic materials dispersed in the environment, in all lands, waters and sediments in layers of earth (Gaffeey, et al, 1996). According to Aiken, et al (1985) there was three major fraction of humic compounds that could be distinguished by their solubility:

1. Humin was the fraction of humic substances that was not soluble in water at all pH values.
2. Humic acid was a fraction of humic substances that was not soluble in water under acidic conditions but soluble at high pH.
3. Fulvic acid was the fraction of humic acid compounds that could dissolved at various pH values.

In environment, humin was largest fraction of humic compounds and relatively easy to get (Stevenson, 1994). Research conducted by Ishiwatari (1985) in some lakes in Japan gave results of 17% humic acid, fulvic acid 11% and 67% humin. Although humic acid and fulvic acid were also influence but humin fraction played an important role because of eosin would interact with organic matter and minerals contained in humin. Based on the idea that humin could be seen as a macromolecular polyelectrolytes insoluble in acidic or alkaline and have a main group -COOH and -OH (phenolic) (Kaled, H., and and Fawy H., A., 2011) so that humin could interact to form a bond with eosin.

Various studies on the interaction of humin with a number of contaminants have been conducted by several experts, especially organic contaminants, such as poliaromatis hydrocarbons (PAHs) and poliklorobifenil (BCBS) which takes place relatively quickly and in some cases irreversible. In this research, we studied the interaction between humin with eosin as an organic compound whose presence in aquatic environments as waste dye

**Research Method**

**Tool and Materials**

The research tool used pH paper, filter paper outstanding, filter paper Whatmant 42, UV-vis spectrometer Hitachi 150-20, infrared spectrometer Shimadzu FTIR-820IPC, shaker, karbolit furnace, appliance titration, pH meter Orion 290A models, sieves, scales digital, dark plastic bottle, flask with various sizes, porcelain bowls, glass tools in Physics Chemistry Lab. and Inorganic Lab. Of Gadjah Mada University

Materials used peat from Pontianak and chemicals compound such as eosin, sodium hydroxide (NaOH) 0.1 M, hydrochloric acid (HCl) 37.5%, hydrochloric acid (HCl) 0.1 M, fluoride acid (HF) 0, 3 M, barium hydroxide (BaOH.8H2O), calcium acetate (Ca(CH3COO)2), hydrochloric acid 0.5% (E merck), N2 gas (PT Samator Gas), CO2-free distillate water and distilled water

**Work Procedures**

1. Humin Isolated
humin isolated by the extraction method used 0.1 M NaOH for 24 hours in a nitrogen atmosphere conditions. To removed inorganic materials such as silica, clay and metal used mixed solution of 0.1 M HCl and 0.3 M HF.

2. Procedure for the determination of ash content in humin
Fifty milligrams neutral humin and humin with purification used HCl / HF put into the porcelain cup and then heated in a furnace (furnace) at a temperature of 750°C for 4 hours. Initial sample weight before and after heated noted. Each sample was carried out with 3 times the measurement (triple).

The content of humin quantitative composition performed in this research was total acidity and content of carboxylate groups. -OH phenolic group was determined by calculated the difference between the total acidity and the content of the -COOH group.

3.1 Determination of total acidity content
One hundred milligrams of humin put in a 100 mL flask and add 20 ml of saturated Ba(OH)\(_2\) while flowing nitrogen gas. After flowing nitrogen gas, flask was closed and shaken for 24 hours at room temperature. Simultaneously performed well against the blank solution that was containing only 20 ml of saturated Ba(OH)\(_2\). The formed suspension was filtered by Whatman filter paper 42. The residue washed with CO\(_2\)-free water destital. The filtrate and wash water were mix and then titrated potentiometrically with 0.1 M NaOH standard solution to pH 9.8. The experiments carried out with two repetitions.

The content of the carboxylic group is determined by the equation:

\[
\frac{(V_b - V_s) \times N \times 10^5 \text{ cmol/kg}}{\text{milligram sampel}}
\]

with:

\(V_b\) = Volume of standard alkaline solution used for titration of the blank
\(V_s\) = Volume of standard alkaline solution used for titration of the sample
\(N\) = Normality of standard alkaline solution

Total acidity (cmol / kg) determined by the equation:

\[
\frac{(V_b - V_s) \times N \times 10^5 \text{ cmol/kg}}{\text{milligram sampel}}
\]

with:

\(V_b\) = Volume of standard solution of acid used for the blank titration
\(V_s\) = Volume of standard solution of acid used for titration of the sample
\(N\) = Normality of standard solution of acid
3.3 Determination of -OH phenolic groups

-OH Phenolic group represents the difference of the total acidity with a -COOH group content so that the content of phenolic OH group can be determined by the equation:

\[-\text{OH Phenolic} = \text{The difference between the total acidity and the -COOH group}\]

4. Determination of optimum pH from eosin adsorption on humin.

Fifty milligrams humin was interaction with 25 ml of eosin solution with a concentration 10 mg/L, the concentration resulted from the dilution of the initial solution with concentration 100 mg/L. The pH was adjusted by the addition of HCl or NaOH to get the initial pH value of 2.0; 4.0; 6.0; 8.0; 10.0; 12.0; and 14.0. The solution that had been regulated pH shaken for 120 minutes and allowed to stand for 24 hours to reach equilibrium. After the interaction, the filtrate and the precipitate separated by filtered. The obtained filtrate analyzed by UV-vis spectrophotometer.

5. Determination of the maximum adsorption time

Fifty milligrams of 50 milligrams humin was interaction with 25 ml of eosin solution with concentration 10 mg/L. Mixture of eosin and humin shaken in optimum adsorption pH with variations time of 2, 4, 6, 8, 10, 12, 15, 30, 60, 90, 120, 150, 180, 210, 240 minutes. After shake, filtrate and precipitate separated by filtered. The obtained filtrate analyzed by UV-vis spectrophotometer to determine eosine concentration.

6. Determination of humin adsorption rate

Graphed eosin adsorbed (mol/L) vs. contact time (minutes) was made after known the optimum time of humin adsorption. Furthermore, determine the adsorption rate of humin used equations that created by Santosa (Anshar, 2014). Humin adsorption rate on the organic compounds we know by made the plot:

\[\frac{\ln\left(\frac{C_{eq}}{C_i}\right)}{t} \text{ vs } \frac{t}{C_A}\]

The equation result generated linear relationship with slope = $K_{1A}$ and intercept = $K_{A}$.

Results and Discussion

1. Humin Characterization

Obtained humin from the extraction of peat soils was characterization used infrared spectroscopy and measured the ash content and the quantitative of the functional groups from humin. From humin infrared spectroscopy characterization give results as shown in Figure 1.
Figure 1. humin Infrared spectra (a) washing with HCl / HF and (b) without washing with HCl / HF

Table 1. Wavelength Infrared humin after washing and before washing with HCl / HF

<table>
<thead>
<tr>
<th>Fungsional Group</th>
<th>Wavelength (cm⁻¹)</th>
<th>Before Washing</th>
<th>After Washing</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH</td>
<td>3425,3</td>
<td>3425,3</td>
<td></td>
</tr>
<tr>
<td>-C-H alifatik</td>
<td>2920</td>
<td>2850,6</td>
<td></td>
</tr>
<tr>
<td>-Si-O</td>
<td>1037,6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-COO⁻</td>
<td>1382,9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C=O dari – COOH</td>
<td></td>
<td>1705</td>
<td></td>
</tr>
<tr>
<td>Influence from Na⁺, Mg²⁺, Ca²⁺ in COO⁻</td>
<td>1377,1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Infrared spectra humin before washing and after washing with HCl/HF showed significant differences as shown in Table 1. Washing process used acid solution (HCl / HF) was cause the release of metals that interact with a group -COO⁻ on humin, this happens because the bond between metal ions with Cl⁻ and F⁻ stronger than the bond between the metal with -COO⁻ group. -COO⁻ Group due to release of metal and then interacted with H⁺ to form -COOH group after humin washed with acid (HCl/HF). Metals release process and the formation of the -COOH group was indicated by the loss of absorption at a wavelength 1382,9 cm⁻¹ and 1377,1 cm⁻¹ and the appearance of absorption at wavelength 1705 cm⁻¹ which was the absorption wavelength of the -COOH group.

The success of the washed process with HCl/HF could detected with IR spectral data as discussed earlier, could also been seen from the changes in ash content, this was due to the ash content had closely related to mineral deposits. More high the mineral content, the higher ash content. Results of the determination of the ash content of humin without washing and the washing HF / HCl are shown in Table 2.

Table 2. The humin ash content without washing, washing with aquades and the washing HCl / HF

<table>
<thead>
<tr>
<th>Washing Steped</th>
<th>ash content(%, b/b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without washing</td>
<td>10,01</td>
</tr>
<tr>
<td>washing with aquades</td>
<td>4,36</td>
</tr>
<tr>
<td>Washing with HF/HCl 3x</td>
<td>1,26</td>
</tr>
</tbody>
</table>

Table 3 shows the quantitative composition of functional groups on the isolated humin performed using potentiometric titration method. This data is needed to determine how many functional groups that exist in humin especially -COOH group and -OH phenolics that can serve as the active sites of metal adsorption.

Table 3. Comparison of content of total acidity, carboxylic groups, and phenolic hydroxyl groups in humin

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Content in humin (cmol/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In This Research</td>
</tr>
<tr>
<td>-COOH</td>
<td>210,0</td>
</tr>
<tr>
<td>-OH phenolic</td>
<td>343,5</td>
</tr>
</tbody>
</table>

2. Humin Interaction with eosin

Effect of pH variation on eosin interaction with humin

From the graph of relationship between pH and eosin concentration that adsorbed in humin (Figure 2) generally indicated that from pH 2 to about pH 8 adsorption rate of eosin was constant tend not undergo significant changes.
Initial concentration of eosin was 10 ppm, solution volume 25 ml, humin weight 50 mg, time interaction was 120 minutes. The optimum adsorption humin against eosin occurred at pH 4. The interaction that occurs in acidic conditions the possibility of an interaction involving hydrogen bonds. This was because the group -COONa and -ONa group of eosin. If the process of dissolution under acidic conditions would hopefully lead to the release of Na\(^+\) ions from each cluster to form a group -COO\(^-\) and -O\(^-\) group, then the group -COO\(^-\) and -O\(^-\) group will bind to H\(^+\) in acidic conditions to form clusters -COOH and -OH at eosin. -COOH Group and -OH of eosin would interact with the -COO\(^-\) group of humin at a pH of about 3-5 for the carboxyl group of humin dissociate and release protons at a pH of about 3.0 to carboxyl ions resulting humin negatively charged compounds.

After pH 4, an increase in pH will cause a reduction of H\(^+\) in solution. So with increasing pH will cause a decrease in the amount of eosin which teradsorp. Decrease the amount of eosin which teradsorp also due to the alkaline conditions will form OH- ions and at a pH of about 9.0 phenolic hydroxy group at humin also began dissociated and negatively charged compounds which produce large. The existence of dissociation of the phenolic hydroxy groups are increasingly making it difficult eosin teradsorp so in this study eosin optimum adsorption occurs at pH 4. In Figure 3 shows how the group -COO\(^-\) and -O\(^-\) may occur in eosin.

**Figure 3. Reaction formation -COO\(^-\) group and –O\(^-\) on eosin**

**Optimization of adsorption contact time humin against eosin**

After knowing the pH optimum for adsorption, the next parameter determined was the optimum contact time between humin with eosin, eosin initial concentration was 10 ppm, a solution of 25 ml volume, weight humin 50 mg, and pH 4. After interaction between eosin and humin the optimum time adsorption obtained when the contact time was 60 minutes at intervals of contact time between 30 minutes until 240 minutes. The results obtained indicate that after 60 minutes of adsorption by humin compounds have experienced saturation and reach equilibrium as shown in Figure 4. This becaused by existing functional groups on the surface of humin has interacted with eosin resulting entirely incapable humin again to tie eosin compound.

**Figure 4. Relations beetwen time and the amount of the eosin adsobrted.**

**Rate constants of Reaction**
From time optimization of data between humin with eosin, the magnitude of the reaction rate constant (k) can be calculated by making the curve $\ln \left( C_0 / C_t \right) / C_t$ opponent $t / C_t$ as in equation:

$$\ln \left( \frac{C_0}{C_t} \right) / C_t = k \cdot \frac{t}{C_t} + K$$

The reaction rate constant (k) was the value of the slope of the curve. Plot the relationship between $\ln \left( C_0 / C_t \right) / C_t$ Vs $t / C_t$ for adsorption of eosin can be seen in Figure 5.

Figure 5. Graph of the relationship between $\ln \left( C_i / C_0 \right) / C_i$ Vs $t / C_i$ from the adsorption of eosin in humin with 10 mg eosin, the initial solution concentration was 10 ppm, the solution volume was 25 mL, and pH 4.

From Figure 5 obtained that k was first order = the slope, which was $8.4 \times 10^{-3}$ min$^{-1}$, with linearity was $R^2 = 0.9845$.

**Conclusion**

Based on the research results obtained we can be prepared following conclusions:

1. Characterization of humin using infrared spectroscopically, showed that prior to leaching with HCl / HF contained absorption peaks at wave numbers around 1382.9 cm$^{-1}$ derived from stalling anionic -COO$^-$ but after washing with HCl / HF absorption was got weaker. Besides appearing on the new absorption peak wave numbers 1705.0 cm$^{-1}$ generated by the C = O stretching vibration of the -COOH group.

2. In this research, the content of phenolic OH at humin amounted 343.5 cmol/kg higher than the carboxylic group at 210 cmol/kg.

3. Adsorption humin against eosin optimum at pH 4 with optimum contact time was 60 minutes.

4. The reaction rate constants for eosin amounted $8.4 \times 10^{-3}$ min$^{-1}$.

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