Study of Adsorption–Desorption on Batik Industrial Dyes (Naphthol Blue Black) on Magnetite Modified Humic Acid (HA–Fe₃O₄)

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1. Introduction

Naphthol blue-black is two typical dyes that are widely used by batik artisans in Indonesia. These dyes are non-biodegradable organic compounds, so it is complicated to degrade in nature. In batik coloring, the dye is only used around 45%, while the remaining 55% will be disposed of as liquid waste. The existence of these compounds in nature can cause environmental pollution, especially the aquatic environment. Therefore, it is necessary to process dyes contained in batik liquid waste before batik waste is discharged into the waters.

Currently, wastewater treatment techniques in the batik industry are being developed, including photocatalysis, electroylsis, nanofiltration, ultrafiltration, and adsorption [1, 2, 3, 4]. Photocatalysis and electroylsis methods are less effective because they require high costs and are difficult to apply. Meanwhile, the nanofiltration method can cause new problems because the adsorbed dyes will accumulate on the adsorbent’s surface. The adsorption method is reported to be quite useful in removing dyes from batik liquid waste. The advantages of the adsorption method are economical and straightforward. It is just that the dye will accumulate on the surface of the adsorbent and become new waste. Thus, it is necessary to conduct further treatment of the adsorbent post adsorption so that the adsorbent does not become waste and cause new problems.

This study reports the use of economical materials and based on natural resources and local minerals in Indonesia to overcome the naphthol blue-black dyes. The material used in this study is humic acid (HA), which is isolated from peat soils originating from Riau, Sumatra. Humic acid has been widely developed and reported as a successful adsorbent for heavy metals [5, 6, 7] and textile dye compounds [8]. Chemically, HA is a macromolecule that is rich in active groups such as carboxylate (–COOH) and hydroxyl (OH) groups, both phenolics and alcohohlates, and quinones [9, 10]. Hence humic acid is thought to have high absorptivity, including naphthol blue-black dyes. To the author’s knowledge, humic acid isolated from Riau’s peat soils in Sumatra has not been much studied as an adsorbent for naphthol blue-black dyes. The selection of humic acid from the isolation of peatlands in Riau, Sumatra, is based on Rahmayanti et al. [10], who reported that the humic acid from the isolation
of Riau peatlands in Sumatra has a higher –OH group content than humic acid from Kalimantan peatlands.

Humic acid has stability at low pH (pH < 3) and dissolves at pH > 3 [9] so that the pH range of adsorption is limited. HA coating on magnetite compounds (Fe₃O₄) can be done so that HA, as an adsorbent, can work over a wider pH range. Another benefit of AH coating on magnetite compounds is that the desorption process can be carried out without filtration and centrifugation because separation can use external magnetic fields to be more environmentally friendly [11, 12]. The coating on Fe₃O₄ is expected to reduce the particle size of the adsorbent produced so that it can increase the adsorption ability of naphthol blue-black dyes.

2. Methodology

2.1. Equipment and Materials

In this study, the humic acid was humic acid from the isolation of peat soils in Riau, Sumatra. The humic acid coating on magnetite was carried out using iron chloride hexahydrate (FeCl₃·6H₂O), iron sulfate hexahydrate (FeSO₄·7H₂O) and sodium hydroxide. The desorption agents used were distilled water and hydrochloric acid. All of these chemicals came from Merck Darmstadt, Germany. The naphthol blue-black dye used was special in the batik industry.

The equipment used in this study was a set of standard laboratory glassware, vacuum pumps, 4800 Thermolyne oven/furnace, BP 110 Sartorius analytical balance, desiccator, Leistungsfreq type sonicator, 70VA generator, Orion 920A pH meter, shaker (Osk), Shimadzu-8201 PC Fourier Transform Infrared (FTIR) spectrophotometer, and Double Beam 1601 PC Shimadzu UV-VIS Spectrophotometer.

2.2. Preparation of magnetite-modified humic acid (HA–Fe₃O₄)

The magnetite modified humic acid preparation was carried out following the method of Rahmayanti et al. [6] with a slight change. 5.56 g (0.01 mol) of FeSO₄·7H₂O was dissolved in 200 mL of distilled water and added to 11.12 g (0.02 mole) of FeCl₃·6H₂O, which was dissolved in 200 mL of distilled water. The solution was heated at 90°C while stirring, then the mixture was added to the NaOH solution set at a pH of 13 and then added with 2 g of humic acid resulting from the isolation of peat soils. The mixture was stirred at 90°C for 60 minutes. Then the mixture was allowed to stand at the same temperature for 60 minutes. The mixture was cooled at room temperature, then filtered, and the precipitate obtained was washed with 100 mL of distilled water six times (with the help of an external magnetic field). Washing precipitates were heated using an oven at 90°C then characterized using XRD and FTIR spectrophotometers.

2.3. Adsorption of naphthol blue-black on HA–Fe₃O₄

Ten mg of HA–Fe₃O₄ was mixed with 10 mL of naphthol blue-black dye solution at pH 2 with varying concentrations of 100, 200, 300, 400, and 500 ppm. The mixture was shaken for 60 minutes then filtered using Whatman filter paper (with the help of an external magnetic field at the bottom of the bottle). The filtrate obtained was then measured for pH, then analyzed using a UV-Vis spectrophotometer.

2.4. Study of adsorption isotherms

The adsorption isotherm models used to explain the pattern of adsorption isotherms in this study are Langmuir and Freundlich isotherm models. The Langmuir adsorption isotherm model can be expressed by equation (1).

\[
\frac{q_e}{q_{max}} = \frac{1}{K_L} + \frac{1}{q_{max}} C_e
\]

The amount of metal adsorbed at the equilibrium state (mg/g) is expressed as \( q_e \). \( C_e \) is the concentration of free metal ions in solution at equilibrium (mg/L). \( q_{max} \) is the maximum adsorption capacity (mg/g), and \( K_L \) is the Langmuir constant (L/mol) related to the adsorption energy [13].

The Freundlich isotherm model is expressed by equation (2).

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

The number of species adsorbed per gram of adsorbent at equilibrium (mg/g) is referred to as \( q_e \). \( C_e \) is the concentration of free metal ions in solution at a state of equilibrium capacity (mg/g). \( K_F \) is the Freundlich constant, which is related to adsorption capacity, and \( 1/n \) is a factor of heterogeneity [14].

2.5. Desorption of Naphthol Blue Black Dyes

The post- adsorption HA–Fe₃O₄ adsorbent was put into distilled water and added by HCl desorption agent with a variation of 0.5 M; 1 M; 1.5 M, and 2 M. The mixture was shaken at 125 rpm for 60 minutes. The solution was filtered for the filtrate then analyzed using a UV-Vis spectrophotometer according to the naphthol blue-black dye wavenumber. Post desorption adsorbents were characterized using FTIR. The percentage of desorption was calculated using the formula presented in Equation 3.

\[
\text{desorption (\%)} = \left( \frac{\text{naphthol blue–black dye}_{\text{initial}} - \text{naphthol blue–black dye}_{\text{remaining}}}{\text{naphthol blue–black dye}_{\text{initial}}} \right) \times 100\%
\]

3. Results and Discussion

3.1. Modification of Humic Acid with Magnetite (HA–Fe₃O₄)

The success of modification of humic acid with Fe₃O₄ was studied using FTIR, and the spectra are presented in Figure 1. The presence of magnetite in humic acid is characterized by adsorption at a wavelength of 580 cm⁻¹, which is the stretching vibration of Fe–O. Meanwhile, the
loss of absorption of the carboxylic group C=O at wavelengths of 1700 cm⁻¹ and 1500 cm⁻¹ indicates that the organic compound's anion binds to the surface of the magnetite through chemical bonds. The possibility is through a carboxylic group that is symmetrically bonded to the magnetite surface, as indicated by the absorption only in the region of 1400 cm⁻¹. Absorption, which shows functional groups of HA, also appears (Figure 1. (c)) even with lower intensity. Thus, it can be said that the modification of humic acid with Fe₃O₄ has been successfully carried out. Evidence of HA-Fe₃O₄ adsorbent having magnetic properties is presented in Figure 2. (a).

The alleged interaction between Fe₃O₄ and HA is through the formation of chelate -COO-Fe (Figure 2) because the modification of HA with Fe₃O₄ is carried out in an alkaline atmosphere (pH 9–10). In this condition, the surface of Fe₃O₄ tends to be negative because the pH > point of zero charges (pHpzc) of Fe₃O₄. Meanwhile, at this pH, the carboxylic and phenolate HA groups have been deprotonated so that interaction between the Fe₃O₄ surface with -COO- and -O- is not possible to occur through electrostatic interactions.

3.2. Study of Naphthol Blue Black Adsorption Isotherms on HA-Fe₃O₄

In this study, the naphthol blue-black adsorption isotherm on HA-Fe₃O₄ was studied through the Langmuir and Freundlich adsorption isotherm models. The Langmuir adsorption isotherm model was determined by making a graph of Ce/qe versus Ce, as presented in Figure 3b. Based on the graph, on the naphthol blue-black adsorption on HA-Fe₃O₄, the correlation coefficient (R²) obtained is 0.996, an adsorption capacity of 0.00241 mol g⁻¹ adsorbent, adsorption equilibrium constant (KL) of 5.9 x 10⁴ L mol⁻¹ and adsorption energy (Eₐ) 26.62 kJ mol⁻¹. Whereas, the Freundlich isotherm model for naphthol blue-black adsorption on HA-Fe₃O₄ was determined by graphing log qe versus log Ce, as presented in Figure 3a. Based on the graph, the correlation coefficient (R²) obtained is 0.906, and the Freundlich (KF) constant is 5.77 x 10⁻² mol g⁻¹.

From Table 2, it can be seen that the adsorption of naphthol blue-black on HA-Fe₃O₄ follows the Langmuir
isotherm model with a correlation coefficient ($R^2$) of 0.996. Thus, the active site on the surface of HA-Fe$_2$O$_3$ can be considered homogeneous. There is no interaction between naphthol blue–black molecules, so it can be said that naphthol blue–black on HA–Fe$_2$O$_3$ only forms one layer (monolayer). When viewed from the adsorption energy ($E_{ads} = 26.64$ kJ/mol), the interaction between naphthol blue–black and HA–Fe$_2$O$_3$ adsorbent is physiosorption. The activation energy in physisorption is in the range of 5–40 kJ/mol, while chemisorption is 40–800 kJ/mol [15]. Compared with some of the results of previous studies (Table 2), it appears that naphthol blue–black dyes can be better adsorbed on HA–Fe$_2$O$_3$ compared to methylene blue and gold dyes in aqueous solutions.

**Table 2.** Calculated values of parameters in Langmuir and Freundlich equations

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Langmuir equation</th>
<th>Freundlich equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA–Fe$_2$O$_3$</td>
<td>$\frac{q_{ads}}{E_{ads}}$</td>
<td>$E_{ads}$</td>
</tr>
<tr>
<td>Black</td>
<td>6.9 x 26.64</td>
<td>0.996</td>
</tr>
<tr>
<td>HA–Fe$_2$O$_3$</td>
<td>1608</td>
<td>18.6</td>
</tr>
<tr>
<td>HA–Fe$_2$O$_3$</td>
<td>1.00 x 0.0034</td>
<td>-</td>
</tr>
</tbody>
</table>

At this pH, the phenolate–OH group protonates to –OH$_2^-$, while the naphthol blue–black group is anionic because it has a –SO$_3^-$ group, so that electrostatic interactions between the adsorbent surfaces and the adsorbate are possible. The second suspicion, interactions occur through hydrogen bonds between the hydrogen atom of the –OH phenolate adsorbent group and the oxygen atom of the naphthol blue–black sulfonate group. The appearance of uptake in the 1010 cm$^{-1}$ and 1066 cm$^{-1}$ regions (Figure 4c) shows the S–O group stretch vibrations and the asymmetric strain S=O groups originating from the sulfonate groups.

3.3. Desorption Study on Naphthol Blue Black Dyes

Desorption studies can be studied using thermal and chemical regeneration methods [16]. In this study, the desorption of naphthol blue–black from HA–Fe$_2$O$_3$ adsorbent was studied using chemical methods with desorption agents as distilled water and HCl. The mechanism of the naphthol blue–black (adsorbate) desorption reaction from HA–Fe$_2$O$_3$ (adsorbent) using an HCl desorption agent is thought to be through an ion exchange reaction. The HCl desorption agent in the solution ionized into H$^+$ and Cl$^-$. The Cl$^-$ ion replaces the adsorbate (which is negatively charged) to bind to the adsorbent, and or the H$^+$ ion replaces the protonated adsorbate (positively charged) to bind to the adsorbate.

Figure 4 shows that the distilled water desorption agent only succeeded in absorbing naphthol blue–black by 0.58%. Meanwhile, the HCl desorption agent succeeded in absorbing the optimum naphthol blue–black at 8.56% at 1 M HCl concentration. Figure 4 shows that if the concentration of HCl> 1 M, desorption decreases. This is presumably because the naphthol blue–black dye is damaged in a solution that is too acidic. The low ability of distilled water and HCl in the absorption of naphthol blue–black from HA–Fe$_2$O$_3$ is suspected because HCl (H$^+$ and Cl$^-$ ions) do not sufficiently break the bonds formed between naphthol blue–black and the surface of the adsorbent HA–Fe$_2$O$_3$. As previously explained, the bond energy formed between naphthol blue–black and the surface of the HA–Fe$_2$O$_3$ adsorbent is 26.64 kJ mol$^{-1}$.

**Figure 4.** FTIR spectra (a) HA–Fe$_2$O$_3$; (b) naphthol blue black; (c) HA–Fe$_2$O$_3$ after adsorption; (d) HA–Fe$_2$O$_3$ after desorption

FTIR data after adsorption (Figure 4) shows that there are differences in uptake that appear before and after naphthol blue–black is adsorbed on HA–Fe$_2$O$_3$. The difference is seen in the absorption that appears in the region of 3500–3200 cm$^{-1}$ and the region of 1000–1100 cm$^{-1}$ (Figure 4c). The absorption that appears in the area of 3400 cm$^{-1}$ has decreased intensity after adsorption. This is presumed because the HA–Fe$_2$O$_3$ phenolate group plays a role in the naphthol blue–black adsorption process on HA–Fe$_2$O$_3$. Interactions that occur are suspected through electrostatic interactions because the adsorption of naphthol blue–black on HA–Fe$_2$O$_3$ is carried out at pH 2.

**Figure 4.** The effect of HCl concentration on desorption efficiency (reaction time 60 min, reaction temperature 30°C)
4. Conclusions

Magnetic modified humic acid (HA–FeO₃) can be used as an adsorbent for dyes in the batik industry liquid waste (naphthol blue–black). The adsorption isotherm study showed that the adsorption of naphthol blue–black on HA–FeO₃ followed the Langmuir isotherm model with adsorption capacity $q_{\text{max}} = 0.00241$ mg/g. Desorption studies show that naphthol blue–black does not succeed in degrading well enough from HA–FeO₃. The efficiency of desorption using distilled water desorption agents is 0.058% while using HCl desorption agents (1 M) is 5.86%.

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