

## Isolation, Characterization and Application of Humin From Riau, Sumatra Peat Soils as Adsorbent for Naphtol Blue Black and Indigosol Blue Dyes

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**ABSTRACT.** Isolation, characterization and application of humin as adsorbent for naphtol blue black (NBB) and indigosol blue (IB) dyes has been carried out. Humin application in this study aims to obtain the optimum pH conditions and kinetics model for adsorption NBB and IB dyes onto humin. Humin was isolated from peat soils originating from Riau, Sumatra. The isolation method used was the alkaline extraction method and the characterization of humin using FTIR spectrophotometer. The total acidity, carboxylic groups and -OH phenolic groups of humin were determined quantitatively using the acid-base titration method. FTIR characterization indicated the presence of an -OH group which was indicated by the appearance of absorption at a wavelength of  $3425.3\text{ cm}^{-1}$  and a stretching vibration of C=O from the -COOH group at a wavelength of  $1705\text{ cm}^{-1}$ . The quantitative calculation of the total acidity value, the content of the carboxylic group and the -OH group phenolics of humin were  $508.47\text{ cmol kg}^{-1}$ ,  $289.42\text{ cmol kg}^{-1}$  and  $219.05\text{ cmol kg}^{-1}$ , respectively. The optimum pH conditions for adsorption NBB and IB onto humin occurred at pH 5 and pH 2, respectively. The adsorption kinetics model of NBB and IB on humin followed the Ho kinetics model.

**Keywords :** isolation, characterization, adsorption, naphtol blue black, indigosol blue

### INTRODUCTION

The use of synthetic dyes in the textile industry raises environmental problems. Synthetic dyes were non-degradable and carcinogenic, causing the dyes to easily accumulate in nature and endanger human health. Several studies related to the processing of NBB and IB dyes using the adsorption method has been reported, including: Rahmayanti, Yunita, & Putri (2020) using a magnetite-modified humic acid adsorbent to adsorb NBB dye. Humic acid isolated from Kalimantan peat soil has been reported to have successfully adsorbed NBB (Prandini, & Rahmayanti, 2020) and IB (Santi, & Rahmayanti, 2019) dyes. Research related to the study of desorption of synthetic dyes has also been reported by several studies, such as the study of the desorption of dye IB (Ekowati, & Rahmayanti, 2019) and NBB (Fuadah, & Rahmayanti, 2019) from humin isolated from Riau peat soil. Latifah and Rahmayanti (2020) reported on the study of IB desorption from magnetite-modified humic acid adsorbents. Based on the research that has been reported, humic acid and humin can be used as adsorbents to reduce the concentration of dye NBB and IB because the active groups -COOH and -OH possessed by humic acid and humin were protonated to  $-\text{COOH}_2^+$  and  $-\text{OH}_2^+$  interacting with NBB and IB dyes (anionic dye) through electrostatic interaction.

Humic acid and humin are the fraction of humic compounds contained in peat soils. Humic acid dissolves in alkaline pH, whereas humin is a fraction of insoluble humic compounds in various pH ranges so that it can be used as an adsorbent for anionic and cationic dyes. Humin has been reported to be used as an adsorbent for rodamine B dye (Nurmasari, Astuti, Umaningrum, & Khusnaria 2014), reactive orange and red dyes (Jesus, Romao, & Araujo, 2011), and methylene blue dye (Anshar, Santosa, & Sudiono, 2015).

Based on literature studies, no previous research has quantitatively reported the -COOH and -OH groups contained in humin isolated from peat soils in Riau, Sumatra. Therefore, in this study, humin was isolated from peat soil of Riau, Sumatra and characterized quantitatively using acid-base titration method. The quantitative test was carried out using the  $\text{Ba}(\text{OH})_2$  and Ca-acetate to determine the total acidity value, carboxylic group and phenolic group of humin. This research also determined the optimum pH conditions for the adsorption of NBB and IB onto humin. NBB and IB are anionic dyes. Adsorption kinetics studies were studied to determine how to model the adsorption kinetics of NBB and IB onto humin. The structure of the compounds NBB and IB were presented in **Figure 1(a)** and **(b)**

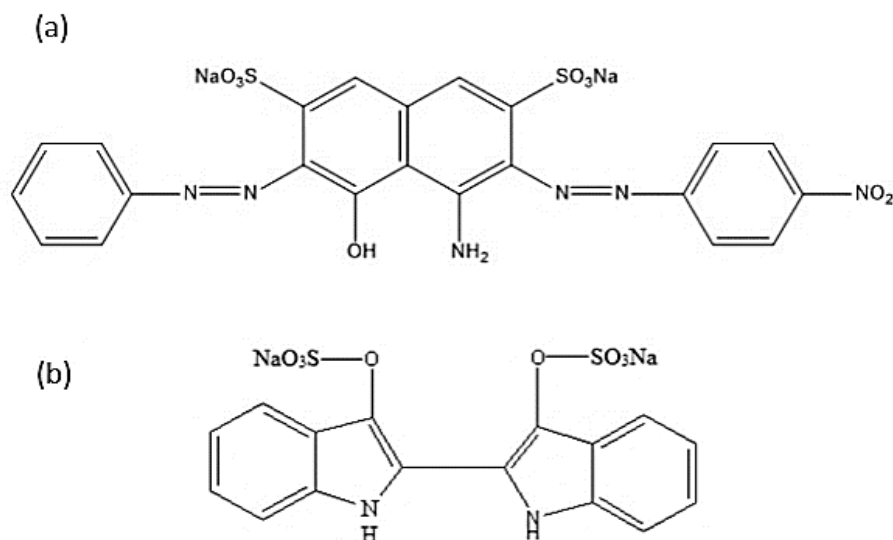


Figure 1. The structure of the compounds (a) NBB and (b) IB

## EXPERIMENTAL SECTION

### Equipment and Materials

The equipments used in this research was a set of standard laboratory glassware, vacuum pumps, Orion 920A pH meter, shaker (Osk), desiccator, Shimadzu-8201 PC Fourier Transform Infrared (FTIR) spectrophotometer, and Double Beam 1601 PC Shimadzu UV-VIS Spectrophotometer.

In this research, the humin isolated from Riau, Sumatra peat soils. The NBB and IB dyes used were widely used in the Yogyakarta batik industry. The chemicals such as sodium hydroxide, hydrochloric acid, barium hydroxide, calcium acetate, fluoride acid from Merck Darmstadt, Germany.

### Isolation of Humin from Sumatran Peat Soil

Humin isolation based on research by Aiken, Mcknight, and Wershaw, (1985). 200 grams of Riau peat soil mixed with 2 L of 0.1 M NaOH. The mixture was stirred using a magnetic stirrer for 24 hours. Furthermore, the mixture was centrifuged at 3000 rpm for 60 minutes. The precipitate was dried using an oven for 30 minutes at 60 °C, then characterized using FTIR.

### Purification of Humin

The precipitate obtained from the previous process was washed 5 times using 0.1 M HCl (250 mL): 0.3 M HF (85 mL) solution. Washing was done with a plastic container by stirring with a magnetic stirrer for 24 hours and leaving it for 12 hours. Furthermore, the mixture was centrifuged at 3000 rpm for 1 hour. The precipitate was rinsed with distilled water and dried in an oven at 60 °C. Then characterized using FTIR.

### Determination of Humin Functional Groups Content

#### Determination of the total acidity of humin

A total of 100 mg of humin was put into an R60 plastic bottle and 20 mL of 0.02 M Ba(OH)<sub>2</sub> solution was added. Prepared a blank solution without the

addition of humin. Blank solution and sample were stirred for 24 hours. The formed suspension was filtered and the residue obtained was rinsed with 20 mL of distilled water. The filtrate and water were mixed and titrated with 0.1 M HCl solution to reach a pH of 8.4.

#### Determination of humin carboxylic group content

A total of 100 mg of humin was put into an R60 plastic bottle then added 10 mL of 0.5 M Ca (CH<sub>3</sub>COO)<sub>2</sub> solution and 40 mL of distilled water. A blank solution was also prepared without the addition of humin. The blank solution and sample were stirred with a stirrer for 24 hours. The formed suspension was filtered and the residue obtained was rinsed with 20 mL of distilled water. The filtrate and water were mixed and titrated with 0.1 M NaOH solution to reach a pH of 9.8.

#### Determination of humin phenolic group

The content of -OH phenolic groups of humin can be determined from the difference between the total acidity and the -COOH groups.

### Adsorption NBB/IB onto Humin

#### Adsorption of NBB And IB onto humin at various pH

A total of 10 mg of humin was put into erlenmeyer and mixed with 10 mL of NBB/IB dye solution with a concentration of 10 mgL<sup>-1</sup> with a variation of pH 2, 3; 4; 5; 6; 7; 8 by shaking for 15 minutes then filtered using Whatman 41 filter paper. The pH of the filtrate obtained was measured, then analyzed by a UV-Vis spectrophotometer according to the maximum wavelength of NBB/IB.

#### Adsorption of NBB And IB onto humin at various reaction time

A total of 10 mg of humin mixed with 10 mL of NBB/IB dye solution with a concentration of 10 mgL<sup>-1</sup> at optimum pH. The mixture was shaken for 3, 6, 9, 12 and 15, 30, 45 and 60 minutes. The mixture was

filtered using Whatman 41 filter paper and then the filtrate was analyzed with a UV-Vis spectrophotometer according to the maximum wavelength of NBB/IB.

## RESULT AND DISCUSSION

### Isolation and Characterization Humin

The peat soil was isolated using an alkaline solution of NaOH, HCl and HF. The isolation was carried out based on the solubility of humin. Humin is a fraction of humic compounds that are insoluble in water at all pH conditions. Extraction was carried out by adding NaOH to dissolve humic acid and fulvic acid which were dissolved in alkaline conditions. The precipitate that was formed was an immature humine compound. The humin then purified using an acid solution of 0.1 M HCl and 0.3 M HF. The HCl and HF separated inorganic contaminants, especially silica and metals from humin, the inorganic components undergo decomposition, so that humin was free from contaminants. After that the resulting precipitate was filtered and dried using an oven at a temperature of 65°C.

Based on Figure 2, the infrared spectra of humin after purification showed several characteristic absorption peaks. The wave number 3425.58 cm<sup>-1</sup> showed the stretching vibration of -OH group, the wave number 1620.21 cm<sup>-1</sup> showed the C=C aromatic stretching vibration conjugating with the other double bonds and the C=O stretching vibration from the -COOH group, at the length waves 2924.09

cm<sup>-1</sup> and 2854.65 cm<sup>-1</sup> showed aliphatic -CH stretching vibrations. In addition, the absorption at the wave number around 1300 cm<sup>-1</sup> was getting weaker and the absorption at the wave number around 1705 cm<sup>-1</sup> was getting sharper.

The FTIR absorption pattern of humin from this research has an absorption pattern that was not much different from the results of research by Anshar et al., (2014). This research was supported by the results of previous research that there was an absorption around a wavelength of 3425.58 cm<sup>-1</sup> which shows a stretching vibration of -OH group, an absorption at a wavenumber of 2924.09 cm<sup>-1</sup> which indicates an aliphatic -CH stretching vibration, a wavenumber of 1620 cm<sup>-1</sup> which indicates the presence of a C = C aromatic bond, the new absorption appears at a wavelength of about 1705 cm<sup>-1</sup> which shows the stretching vibration of C = O from the -COOH group. This absorption arises as a result of the purification process using HCl and HF solutions, where the minerals that bind to the -COO<sup>-</sup> ion are released and replaced by H<sup>+</sup> ions produced from the HCl or HF solution then form -COOH, so it can be assumed that humin isolation has been successfully purified (Nurmasari, et al., 2014). However, the spectra of the inorganic part at a wavenumber smaller than 1000 were still unchanged. It was suspected that the impurity concentration in the form of inorganic compounds was so small that it cannot be read by the FTIR spectrophotometer.

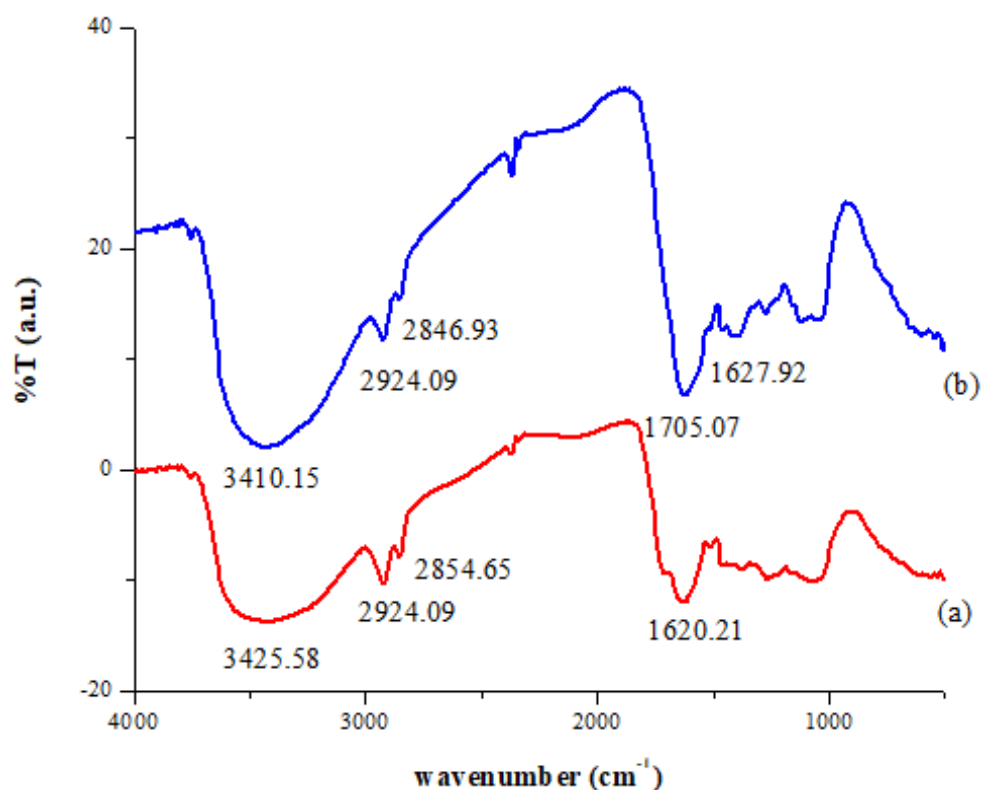


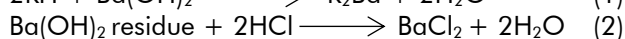
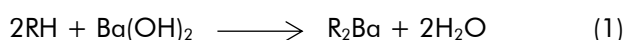
Figure 2. FTIR spectra of isolated humin (a) before purification(b) after purification

### Functional Groups Content of Humic Acid

The content of functional groups of humic acid was carried out by calculating the total acidity, the -COOH group content, and the total -OH content of humic acid.

#### The total acidity of humic acid

The total acidity of humic acid was due to the presence of H<sup>+</sup> in the carboxylate and phenolic groups. Total acidity was determined using the Ba(OH)<sub>2</sub> method by indirect potentiometric titration. The use of the Ba(OH)<sub>2</sub> method produces a higher acidity value than the KOH, NaOH or other methods. This method was based on removing H<sup>+</sup> from the -COOH and -OH groups through the reactions in equations 1 and 2:

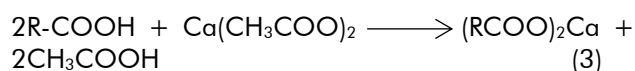


Based on the reactions of equations 1 and 2, R was considered a humic acid macromolecule and H was an H<sup>+</sup> from the -COOH and -OH groups by Ba(OH)<sub>2</sub>. The excess base was titrated using HCl and the result of the titration was used to calculate the total acidity using the formula:  $((V_b - V_s) \times N \text{ HCl} \times 10^5) / \text{mg sample (cmol kg}^{-1})$ , where V<sub>b</sub> and V<sub>s</sub> respectively were the volume of the standard HCl solution used to titrate the remaining Ba(OH)<sub>2</sub> on blank and sample, N is the normality of the HCl solution. The total acidity value of humic acid in this study was presented in **Table 1**. Based on **Table 1**, it can be seen that the total humic acid

value resulted from this study, namely the humic acid isolated from Riau, Sumatran peat soil was smaller than the total acidity value of humic acid isolated peat soil in South and West Kalimantan.

#### Humic acid carboxylic group content

The content of the -COOH group can be determined by the Ca-acetate method, this method was based on cation exchange and uses an indirect potentiometric approach (Stevenson, 1994). The reaction that occurs was presented in equation 3.



This method was based on cation exchange where the -COOH content was determined by titration of acetic acid by NaOH and is calculated using the formula  $((V_b - V_s) \times N \text{ HCl} \times 10^5) / \text{mg sample (cmol kg}^{-1})$ , where V<sub>b</sub> was the volume of the NaOH standard solution used to titrate the blank solution and V<sub>s</sub> was the volume of the NaOH standard solution used to titrate the sample solution. The carboxylic group content of humic acid in this study was presented in **Table 2**. Based on **Table 2**, it can be seen that the content of carboxylate groups in humic acid resulting from the isolation of peatlands of Riau Sumatra was greater than the content of carboxylate groups in humic acid from the isolation of peat soils of South and West Kalimantan.

**Table 1.** The Value of Total Humic Acid from Various Studies

	The Value of Total Humic Acid (cmol kg <sup>-1</sup> )	
This research, Humic acid from Riau, Sumatran Peat Soils	Anshar et al., (2014) Humic acid from South Kalimantan Peat Soils	Dewi, Santosa, & Siswanta (2010) Humic acid from West Kalimantan Peat Soils
508.47	553.50	525.56

**Table 2.** Humic acid Carboxylic Group Content from Various Studies

	The Content of the -COOH Group (cmol kg <sup>-1</sup> )	
This research, Humic acid from Riau, Sumatran Peat Soils	Anshar et al., (2014) Humic acid from South Kalimantan Peat Soils	Dewi, Santosa, & Siswanta (2010) Humic acid from West Kalimantan Peat Soils
289.42	210.00	251.15

**Table 3.** Humic acid Carboxylic Group Content from Various Studies

	The Content of the -OH Group (cmol kg <sup>-1</sup> )	
This research, Humic acid from Riau, Sumatran Peat Soils	Anshar et al., (2014) Humic acid from South Kalimantan Peat Soils	Dewi, et al., (2010) Humic acid from West Kalimantan Peat Soils
219.05	343.5	274.41

**Table 4.** The comparison of the functional groups of humic acid and humic acid from Riau, Sumatran peat soils

Functional Group	Humic acid (This Research)	Humic acid (Rahmayanti, Yunita & Prandini, 2019)
The Total Acidity	508.47	710.00
Carboxylic Group Content	289.42	260.00
phenolic group content	219.05	450.00

### Humin Phenolic Group Content

Humin phenolic group content was calculated from the difference in total acidity with the carboxylate group. The phenolic group content of humin in this study was presented in **Table 3**. Based on **Table 3**, it can be seen that the content of phenolic groups in humin from peat isolation results from Riau Sumatra's peat soils was smaller than the content of carboxylate groups in humin from the isolation of peat soils of South and West Kalimantan.

Based on the total acidity value, the content of carboxylic groups and humin phenolics, showed that humin from the isolation of Sumatran peat soils (this study) has a higher content of carboxylate groups than the content of phenolic groups. Its carboxylic group content was also higher than that of the humine carboxylate group isolated from the peat soil of Kalimantan. Meanwhile, humin from the isolation of Sumatran peat soils (this study) has a lower content of phenolic groups compared to humin from Kalimantan peat soils. Similar to humic acid, the content of carboxylic and phenolic groups of humin affects its ability as an adsorbent. Carboxylic groups and phenolic groups were active sites that play a role in interacting with adsorbates (Rahmayanti et al., 2020). The comparison of the functional groups of humic acid and humin from Riau, Sumatran peat soils is presented in **Table 4**. When compared to humic acid, humin has a much lower total acidity, but the content of carboxylic groups was higher than the carboxylic groups contained in humic acid.

### Application of Humin From Sumatran Peat Soils as Adsorbent for NBB dan IB Dyes

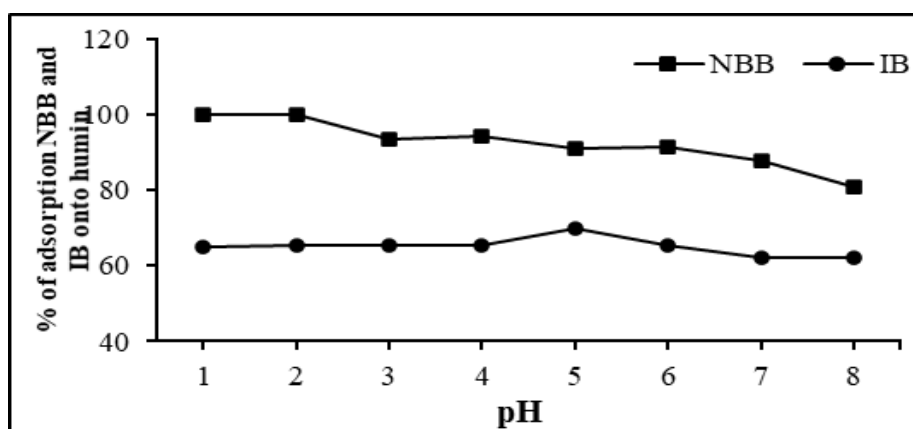
#### The Effect of Acidity on the Adsorption of NBB and IB onto Humin

The interaction between the -COOH and -OH groups of humin and the adsorbate through several processes, including: electrostatic interactions, hydrogen bonding, ion exchange and chelation formation (Aiken, et al., 1985). The interaction between humin adsorbent and adsorbate through electrostatic interaction is strongly

influenced by the acidity of the solution with the following explanation: at low pH, -COOH and -OH groups of humin undergo protonation to produce -COOH<sub>2</sub><sup>+</sup> and -OH<sub>2</sub><sup>+</sup> causing the surface of humin to be positively charged.

This condition allowed the humin adsorbent to interact with the adsorbate which was negatively charged through electrostatic interaction. In this, it was seen that the adsorption of NBB and IB on humin was influenced by pH but not significantly. Based on **Figure 3**, the adsorption of NBB and IB on humin was optimum at pH 2 and 5, respectively. The percent change of adsorption NBB and IB onto humin in the pH range 1-8 was 80-100% and 62-70%, respectively. This showed that the interactions that occur in NBB and IB with humin were not only through electrostatic interactions. If only through electrostatic interactions, when the pH was alkaline, the surface of the humin would be negative because the -COOH and -OH groups deprotonated to produce -COO<sup>-</sup> and -OH<sup>-</sup>. This condition caused the humin adsorbent to be more difficult to interact with NBB and IB which were anionic dyes. Based on this study (**Figure 2**), at pH 7 and 8, NBB and IB could still be adsorbed onto humin with the percent of adsorption were > 80% and > 60%, respectively.

Another suspected interaction that occurs between humin and NBB or IB was through hydrogen bonding. This assumption was reinforced by a higher adsorption percent of NBB onto humin (100% at pH 2) compared to adsorption percent of IB onto humin (70% at pH 5). This result can be explained as follows: NBB was a dye with more varied functional groups compared to IB. NBB has functional groups -SO<sub>3</sub><sup>-</sup>, -OH, -NO<sub>2</sub>, -NH<sub>2</sub> and N=N, while IB has -SO<sub>3</sub><sup>-</sup> and -NH functional groups. The difference in the types of functional groups caused NBB would be easier to interact with humin than IB, through hydrogen bonding. If only through electrostatic interactions, the optimum pH of IB adsorption on humin will also occur at pH < 5, because at lower pH the surface of humin was more positive.



**Figure 3.** Percent of adsorption NBB and IB onto humin at various of pH (contact time = 60 minutes, initial concentrations of the dyes = 25 mgL<sup>-1</sup>)

**The Adsorption Kinetics Model of NBB and IB onto Humic**

The adsorption kinetics models of NBB and IB onto humin used in this study were Lagergren's pseudo-first-order kinetics model (Ho, 2004) and Ho's pseudo-second-order kinetics model (Ho and McKay, 1999). Lagergren's pseudo first-order kinetics model was expressed by equation (4).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

Based on equation (4), the amount of NBB/IB concentration adsorbed per unit mass of humin adsorbent at time "t" is expressed as (mg.g<sup>-1</sup>) and the amount of NBB/IB concentration adsorbed per unit mass of humin adsorbent at equilibrium has been reached stated with (mg.g<sup>-1</sup>). The Lagergren adsorption rate constant was expressed as k<sub>1</sub> (minute<sup>-1</sup>). The application of the Lagergren kinetics model was carried out by creating a curve t versus ln q<sub>e</sub>-q<sub>t</sub> that produces slope and intercept, adsorption rate constant (k<sub>1</sub>) = - slope, and the amount of NBB/IB adsorbed on humin at equilibrium obtained from the intercept, where the intercept = ln q<sub>e</sub>.

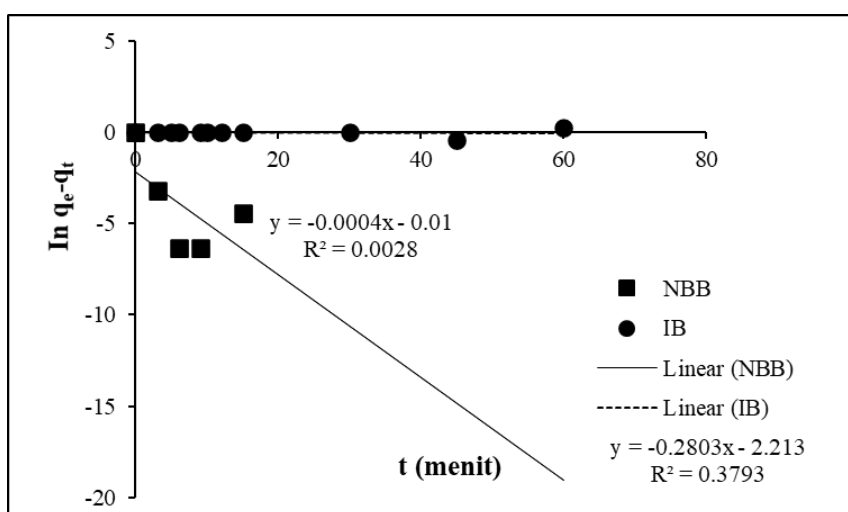
Curve of NBB and IB adsorption onto humin based on Lagergren's pseudo first-order kinetics equation were presented in Figure 4. Based on Figure 4, it was obtained that the R<sup>2</sup> value was very small for both the adsorption of NBB and IB onto humin. Thus, the adsorption of NBB and IB dyes onto humin did not follow Lagergren's pseudo first order kinetics model. Pseudo first order kinetics model was widely assumed from the presence of the adsorption mass action rate which involves diffusion in the surface layer of the adsorbent as the main determinant of the adsorption rate. This means that the adsorption of NBB and IB onto humin in this study was not only determined by the proportion of humin adsorbent only. Another assumption was that the initial concentrations of NBB and IB solutions used in this study were not excessive compared to the availability of active sites on the

humic adsorbent. This was in accordance with what was reported by Santosa (2014). This kinetics model was limited to use for adsorption with an initial concentration of adsorbate solution that is more than the availability of active sites on the adsorbent.

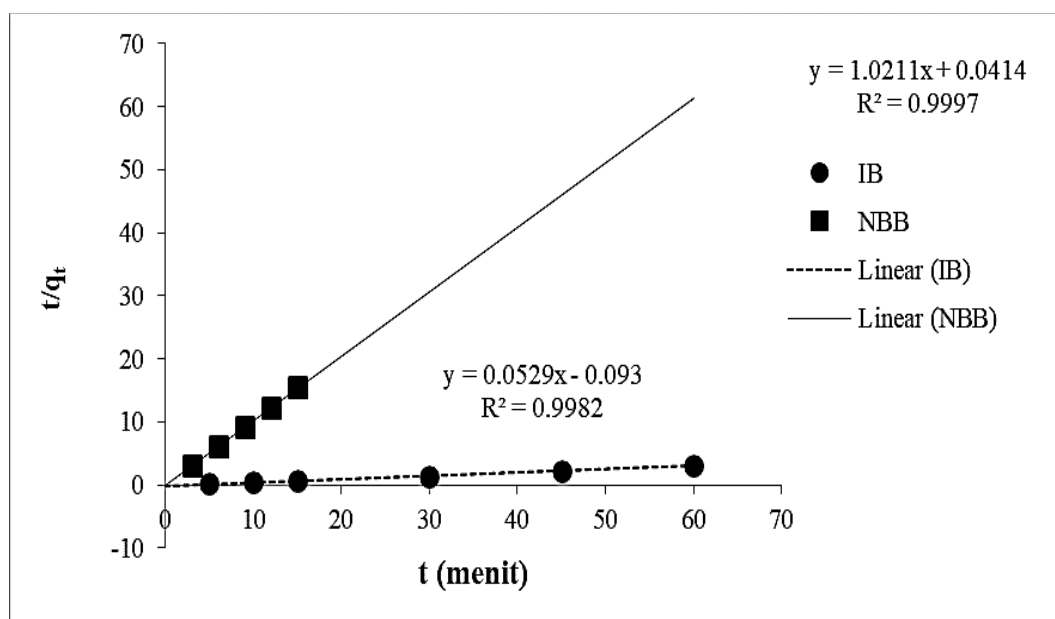
Ho's pseudo second-order kinetics model was expressed by equation (5).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (5)$$

The adsorption rate constant Ho was expressed as k<sub>2</sub> (g.mg<sup>-1</sup>.min<sup>-1</sup>), q<sub>e</sub> and q<sub>t</sub> are the amount of NBB/IB concentration adsorbed per unit mass of humin adsorbent at time "t" and at equilibrium was reached in units of mg.g<sup>-1</sup>. The application of the Ho kinetics model was carried out by making a curve t (minutes) versus t/q<sub>t</sub> which results in slope = 1/q<sub>e</sub> which was used to calculate the adsorption capacity of the dye NBB/IB onto humin at equilibrium, and the intercept = 1/(k<sub>2</sub>q<sub>e</sub><sup>2</sup>) which was used for calculate the adsorption constant Ho (k<sub>2</sub>). The initial adsorption rate (h) was obtained from the value 1/intercept. Curve of NBB and IB adsorption onto humin based on Ho's pseudo second-order kinetics equation were presented in Figure 5. Based on Figure 5, the R<sup>2</sup> values on the NBB and IB adsorption curves onto humin were 0.9997 and 0.9982, respectively. This means that the adsorption of NBB and IB onto humin adsorbent follows the Ho kinetics model. These results were the same as the results of research by Rahmayanti et al. (2020) which conducted a study of the adsorption kinetics of NBB and IB on humic acid. The Ho kinetics model assumes that the adsorption capacity was proportional to the number of active sites of the adsorbent. That is, the adsorption capacity of NBB and IB onto humin was proportional to the number of active sites of humic adsorbent (Ho, & Mc Key, 1999). Comparison of the parameters of the Ho adsorption kinetics model for the adsorption of NBB and IB onto humin was presented in Table 5.



**Figure 4.** Adsorption of NBB and IB onto humin based on Lagergren's pseudo first-order kinetics equation (room temperature, pH = 2 (NBB), pH = 5 (IB))



**Figure 5.** Adsorption of NBB and IB onto humin based on Ho's pseudo second-order kinetics equation (room temperature, pH = 2 (NBB), pH = 5 (IB))

**Table 5.** Comparison of the Ho adsorption kinetics model parameters for the adsorption of NBB and IB onto humin

Adsorbate	Ho's pseudo second-order kinetics model			
	R <sup>2</sup>	q <sub>e</sub> (mmol/g)	h (mmol/g.minute)	K (g/mmol.minute)
NBB	0.9997	0.979	24.155	25.185
IB	0.9982	0.969	0.551	0.5861

Based on **Table 5**, it can be seen that the adsorption rate constants (k) and initial adsorption rates (h) for NBB adsorption onto humin were higher than the adsorption constants IB onto humin. Likewise, the adsorption capacity of NBB at equilibrium was higher than the adsorption capacity of IB at equilibrium. This was thought to be influenced by differences in the molecular structure of NBB and IB as described in the previous section. The more diverse active sites of the NBB cause interactions between NBB and humin to occur more quickly. However, to determine the maximum adsorption capacity of NBB and IB in humin, it is necessary to study the adsorption isotherm.

## CONCLUSIONS

Humin has been isolated from Riau Sumatran peat soils using the alkaline extraction method. The total acidity, carboxylic and phenolic groups content of humin -OH groups were 508.47 cmol kg<sup>-1</sup>, 289.42 cmol kg<sup>-1</sup> and 219.05 cmol kg<sup>-1</sup>, respectively. The optimum pH conditions for adsorption of NBB and IB onto humin occurred at pH 5 and pH 2, respectively, with % adsorption of NBB and IB onto humin was 100% and 70%, respectively. The adsorption kinetics model of NBB and IB onto humin followed the Ho kinetics model.

## ACKNOWLEDGMENTS

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