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Adsorption of Congo Red onto Humic Acid Isolated from Peat Soil Gambut Regency, South Kalimantan

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ABSTRACT. Humic acid is one of the green materials for wastewater treatment including for removal dyes as an adsorbent. Humic acid was isolated from peat soil, Gambut Regency, South Kalimantan following International Humic Substances Society method, and used to adsorb Congo red. The adsorption process was carried out in a batch system and the effect of pH, contact time, and adsorption capacity of Congo red on humic acid were studied. The adsorbent characterization by using FTIR. The results showed that the adsorption of Congo red on humic acid occurred at the optimum pH of pH 6, the optimum contact time was 120 minutes. The adsorption capacity of Congo red onto humic acid of 33.33 mg/g and follows the Langmuir model with R^2 = 0.9926. The characterization of humic acid functional groups before and after adsorption of Congo red showed that the signal at 1,712.79 cm^{-1} were shifted to 1,705.07 cm^{-1} and 1,273.02 cm^{-1} were shifted to 1,265.30 cm^{-1}. These suggested that the mechanism interaction was the electrostatic interaction between $-NH^{3+}$ functional group of Congo red group and $-COO^{-}$ functional group of humic acid. It means that humic acid isolated from peat soil could be used as an adsorbent for the removal Congo red.

Keywords: Adsorption, congo red, contact time, humic acid, pH

INTRODUCTION

Industrial activities such as textile, dyeing, food processing, paint, printing, paper, and plastic used approximately 50%. It was estimated 10-20% was lost during the dyeing process and released as wastewater (Alver & Metin, 2012; Fan et al., 2006; He et al., 2007; Sharma & Janveja, 2008). Anionic dyes were unaffected by light, water, photodegradation, biodegradation, oxidizing agents, and heat (Ayawei et al., 2015; McKay et al., 1981; Nagda & Ghole, 2009; Sharma & Janveja, 2008). Therefore, it was difficult to degrade it even at low concentrations. The presence of dyes in aquatic can affect aquatic life and the food chain by reducing the intensity of sunlight transmission, so that the photosynthesis process can not occur optimally, dissolved oxygen (DO) was reduced (Chen & Chen, 2018; Foroutan et al., 2020; Ma et al., 2011). Congo red is the most anionic dye widely used in the textile industry. In humans, Congo red that accumulates in the body can cause impaired liver, respiratory, kidney, nerve, skin irritation, and cancer (Jiang et al., 2019; Tang et al., 2019; Zhang et al., 2018)

Many methods have been developed for dyes removal both physically, biologically, and chemically such as coagulation or flocculation (Nourmoradi et al., 2016; Rodrigues et al., 2013; Tarchitzky et al., 2017), oxidation (Islam et al., 2019), nanofiltration (Liu et al., 2017), electrochemistry (Baddouh et al., 2020), degradation (Fahimirad et al., 2017), microbial degradation (Kadam et al., 2013), electrochemical degradation (Fan et al., 2006), etc. These techniques have disadvantages such as using chemicals in large quantities, producing amounts of sludge, high operational costs, limited application, and need a long process (Huang et al., 2018; Kundu et al., 2006). However, adsorption is one of the best and efficient methods for removing dyes from water. It is because the easy design and operation, without sludge formation, inexpensive, has great effectiveness, does not cause new problems in the environment (Daoud et al., 2019; Silva et al., 2013).

Several materials, including modified activated carbon, silica, zeolite, chitosan, fly ash, clay, graphene have been used as an adsorbent (Naushad et al., 2019; Tarchitzky et al., 2017). However, these materials are relatively expensive, thus motivating researchers to look for cheaper and more efficient adsorbents. Humic acid is the main natural organic material in soil as well as in geological organic

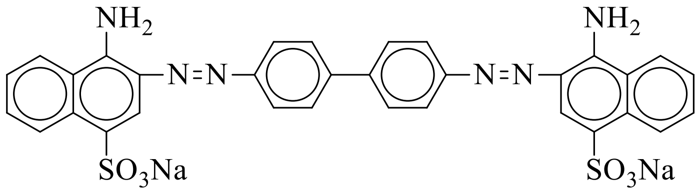

Figure 1. Structure of Congo red

deposits. Humic acids have many functional groups including carboxyl, phenolic, hydroxyl, carbonyl, methoxyl, ether, and amino groups in their skeleton. The binding capacity of carboxylic and phenolic groups through electrostatic interactions, hydrogen bonds, dipole interactions that efficiently remove organic pollutants such as dyes in water (Chianese et al., 2020; Sun et al., 2015). In this research humic acid was isolated from peat soil, Gambut District, South Kalimantan, and used as an adsorbent to remove Congo red dye from an aqueous solution by the batch system. This research aimed to investigate the effect of pH, contact time, and adsorption capacity of Congo red onto humic acid. The adsorption performance was examined by the Langmuir and Freundlich model. Lastly, the characterization of humic acid before and after adsorption will be conducted and analyzed by FTIR. The data obtained will be a reference in future research to modify humic acid in adsorption of congo red. The structure of Congo red was presented in **Figure 1**.

EXPERIMENTAL SECTION

Materials and Instrumentation

The reagents used in this research include: HCl, HNO_3, HF, CH_3COOH, NaOH were purchased from Merck. Congo red was purchased from Sigma Aldrich. Sample characterization using UV-Vis Spectrophotometer *Gold Spectrumlab* and Fourier Transform Infrared Spectroscopy (FTIR) *Shimadzu 8201PC*.

Adsorbent preparation

Humic acid (HA) was isolated from peat soil, Gambut District, South Kalimantan following the method recommended by the International Humic Substances Society (IHSS) (Tarchitzky et al., 1993) with some modification (Santoso & Herdiansyah, 2004).

The modifications were included extracting for 24 hours after adding 1M NaOH and standing for 16 hours after adding HCl. After being obtained, the humic acid solid was placed in a plastic container with a solution of 0.1 N HCl and 0.3 N HF and then shaken for 20 hours at room temperature. The precipitate formed was rinsed with distilled water until the rinse water was free of Cl^- (tested with $AgNO_3$ solution). This purification process was carried out 2 times.

Congo red Adsorption Experiment

Congo red stock solution 1,000 mg/L was prepared by dissolving 1 gram Congo red into 1,000 L distilled water. A number of Congo red standard solution were made from stock solution in concentration 5 to 25 mg/L. Congo red adsorption was examined using batch system. In general, the adsorption experiments was carried out by adding 0.1 gram HA sample into 50 mL of 100 mg/L Congo red solution in Erlenmeyer flask. Then, the adsorption was carried out at various time from 10 to 210 minutes to get an optimum time adsorption. The filtrate was filtered with filter paper (Whatman 42) and the filtrate concentration was determined using UV-Vis Spectrophotometer *Gold Spectrumlab* at the maximum wavelength (λ_{max}) 497 nm. The effect of pH on the Congo red adsorption was studied by adjusting pH from 5 to 9. Percentage adsorption of Congo red was calculated using the equation 1.

$$\%\, adsorption\ congo\ red = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where C_0 is the initial of Congo red concentration (mg/L), C_t is the concentration of Congo red at any time (mg/L).

The kinetic study of adsorption of Congo red onto HA was carried out by adding 0.1 gram HA sample into 50 mL of 25, 50, 75, 100 and 125 mg/L Congo red solution in Erlenmeyer flask and shake at optimum time. The filtrate was filtered with filter paper (Whatman 42) and the filtrate concentration was determined using UV-Vis Spectrophotometer *Gold Spectrumlab* at the maximum wavelength (λ_{max}) 497 nm. The kinetic data was calculated based on Langmuir and Freundlich isotherm model.

RESULTS AND DISCUSSION

FTIR Characterization of Humic Acid

The adsorption capacity was influenced by the adsorbent functional group. The functional groups in humic acid were determined using FTIR to find out what functional groups might bind to Congo red. According to Stevenson (1994), humic compounds have major functional groups such as –OH. –COOH, quinone, aromatic and aliphatic. Based on the IR spectrum in **Figure 1**, the strong absorption broadband at 3402.43 cm^{-1} indicating the –OH stretching vibration. The occurrence of absorption in the –OH range is a characteristic of humic compounds due to the presence of functional groups of –OH phenolic and –OH alcoholic.

Another characteristic broadband at 2924.09 and 2854.65 cm^{-1}. This band looks very significant in humic acid because it is an asymmetrical or symmetrical vibrational range, especially in the aliphatic C-H range in the active methyl or methylene group which is usually in the form of conjugated ketones with a structure as CO-CH_2-CO-. The peak at 1712.79 cm^{-1} indicates a stretching vibration of C=O which is also one of the characteristics of the infrared spectra of humic compounds and this C=O vibration can come from the ketone, carboxylate, or quinone groups(Stevenson, 1994). The aromatic group was indicated by the presence of weak broadband at 1620.21 cm^{-1} as -C=C- aromatic and conjugated H from ketones. The broadband at 1381.02 cm^{-1} was identified due to the presence of C-O alcohol groups. The broadband at 1273.02 and 1226.73 cm^{-1} show C–O and –OH stretching vibrations from the –COOH group of carboxylic acids. The broadband at 2337.72 and 1126.43 cm^{-1} indicates the –OH group of a secondary alcohol. The broadband at 1381.03 cm^{-1} shows the shape change of the CH_3 curve or the stretching vibration of C–O alcohol.

The characteristic spectra of humic acid are indicated by the appearance of broadband around the wavenumbers of 3,400; 2,900; 1,720; 1,600 and 1,200 cm^{-1}. In general, the comparison of humic acid spectra isolated from peat soil and the theoretical according to Stevenson (1994) can be seen in **Table 1**.

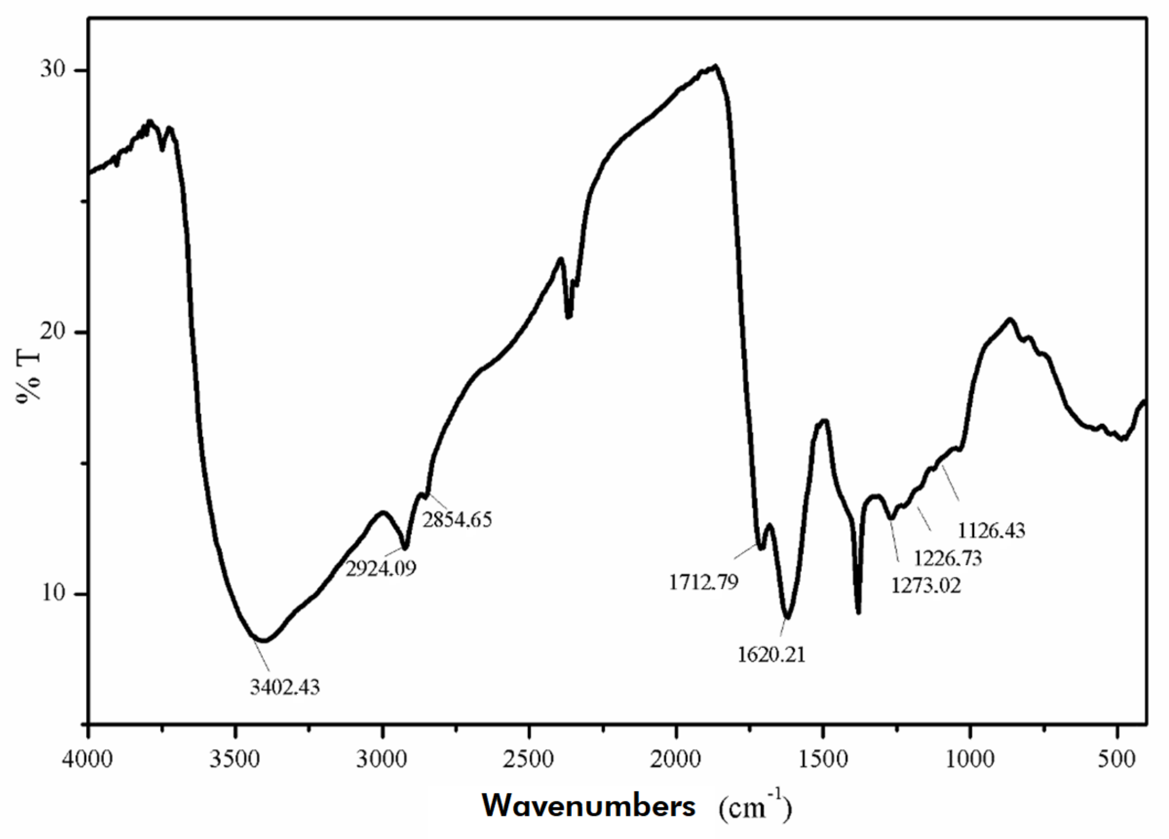

Figure 1. FTIR spectrum of isolated HA

Table 1. Humic acid spectra isolated from peat soil, Gambut Regency, South Kalimantan and theoritical humic acid spectra

Fungsional Groups	Wavelength (cm^{-1})	
	Humic acid isolated	Humic acid theoritical*
-OH from –COOH	3402,43	3400
-C-H aliphatic	2924,09	2900
-C=O from –COOH	1712,79	1720
-C=C aromatic and or H conjugated of ketone	1620,21	1600
-OH from –COOH	1226,73	1200

*Stevenson, 1994

Effect of pH

Determination of the optimum pH for adsorption of congo red onto humic acid aims to determine the pH of the adsorption process of congo red by humic acid which is the highest. The initial pH range of 5, 6, 7, 8, and 9 was used to determine the ideal pH for congo red adsorption by humic acid. Congo red adsorption onto humic acid will be influenced by the pH as shown in **Figure 2**. **Figure 2** shows that pH 6 was selected as the optimum pH for the next stages with percentage adsorption of 41.92 %. This is because at pH 6 (slightly acidic conditions), with the addition of H^+, the Congo red tends to be partially positively charged (NH_3^+), which will result in ionic bond with the negatively charged surface of the humic acid adsorbent (COO^-). Under acidic conditions, the $-NH_2$ group of Congo red will be protonated to $-NH_3^+$ according to this reaction.

$$-NH_2 + H^+ \rightarrow -NH_3^+ \qquad (2)$$

The excess proton in $-NH_3^+$ will be stabilized by the aromatic structure through the delocalization process. This process causes hydrophobic interactions between the aromatic rings in the Congo red molecules, forming an overlap, causing aggregation. This aggregation begins to form when shaken is carried out. According to Fessenden and Fessenden (1985), the $-SO_3Na$ group in water will be ionized to $-SO_3^-$ and Na^+, in the presence of excess H^+ will become $-SO_3H$. This situation will cause a decreased solubility of Congo red in the water. Both of the above (aggregation and decreased solubility) caused the adsorption of Congo red to be low at pH below pH 6.

With an increase pH, under alkaline conditions, $-SO_3Na$ group of Congo red will ionize to $-SO_3^-$ and Na^+, while -COOH and -OH phenolic group of humic acid tend to release proton and form -COO- and $-RO^-$. Therefore, repulsive forces exists between adsorbent and adsorbate and these forces decreased the Congo red adsorption onto humic acid.

Effect of Contact Time

Variation of contact time was carried out to determine the length of time required for the optimum adsorption process of congo red onto humic acid to occur at an optimum pH of 6. The optimum contact time for congo red adsorption by humic acid was determined at intervals of 10, 15, 30, 60, 90, 120, 150, 180, and 210 minutes. **Figure 3** shows that the percentage adsorption increased with contact time from 10 to 120 minutes and became almost constant after 120 minutes to 210 minutes. This is probably due to the vacant site on the adsorbent were filled by Congo red and then the Congo red molecules slowly diffused into the adsorbent surface. Thus, the contact time of 120 minutes was chosen for the next stage with percentage adsorption of 42.12%.

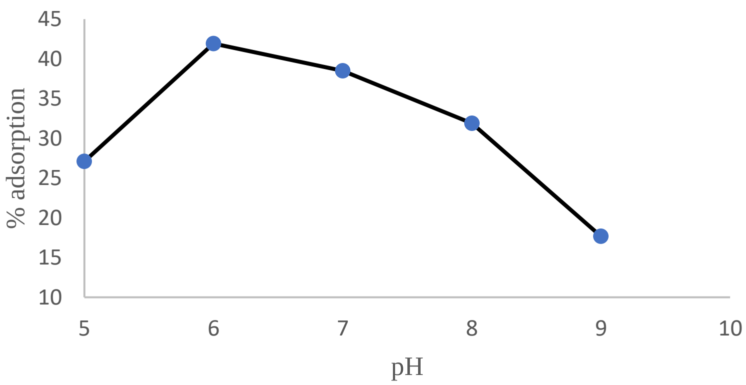

Figure 2. Effect pH Congo red adsorption

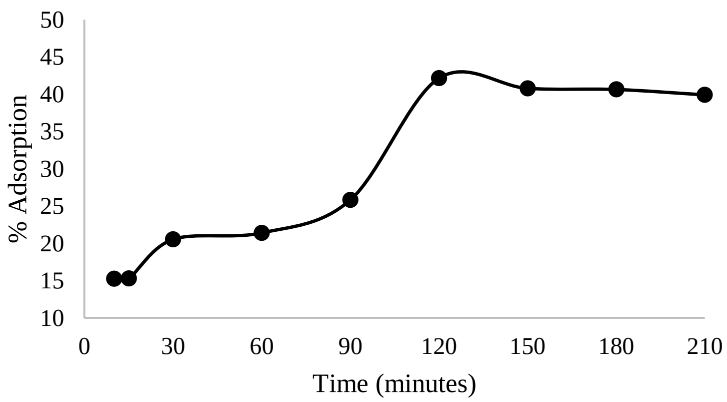

Figure 3. Effect contact time Congo red adsorption

Adsorption Isotherm

Adsorption isotherm model was carried out to describe the adsorption process of dyes onto adsorbent. There are two major adsorption isotherm types: the Langmuir and the Freundlich isotherms. The Langmuir isotherm equation :

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (4)$$

Whereas,
q_e = the amount of adsorbat that adsorbed (mg/g)
C_e = concentration of the congo red solution at equilibrium (mg/l)
K_L = Langmuir constanta
q_{max} = optimum adsorption capacity (mg adsorbat/q adsorbent)

The Freundlich isotherm equation :

$$\text{Log } q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Whereas,
q_e = the amount of adsorbat that adsorbed (mg/g)
C_e = concentration of the congo red solution at equilibrium (mg/l)
K_L and $1/n$ = Freundlich adsorption capacity and adsorption intensity constanta

Moreover, it essential to predict the maximum adsorption capacity. Congo red with a concentration of 25 to 125 mg/L, optimum pH 6 and optimum contact time of 120 minutes were used to determine the adsorption capacity. **Table 2** show that the initial concentration of Congo red with % adsorption optimum at 25 ppm of 80%.

Table 2. Variation of initial concentration Congo red

Co (ppm)	Ce (ppm)	Ca (ppm)	%Ca	qe	Ce/qe
25	5.16	20.66	80,00	10,33	0,49
50	14.26	36.79	72,05	18,39	0,77
75	27.63	48.19	63,55	24,09	1,14
100	49.16	52.12	51,46	26,06	1,88
125	67.33	58.01	46,28	29,00	2,32
150	93.04	59.27	38,91	29,63	3,13

Co = Congo red concentration at inial (ppm)
Ce = Congo red concentration at equilibrium (ppm)
Ca = Congo red concentration adsorbed (ppm)
qe = The amount of adsorbed Congo red dye (mg)

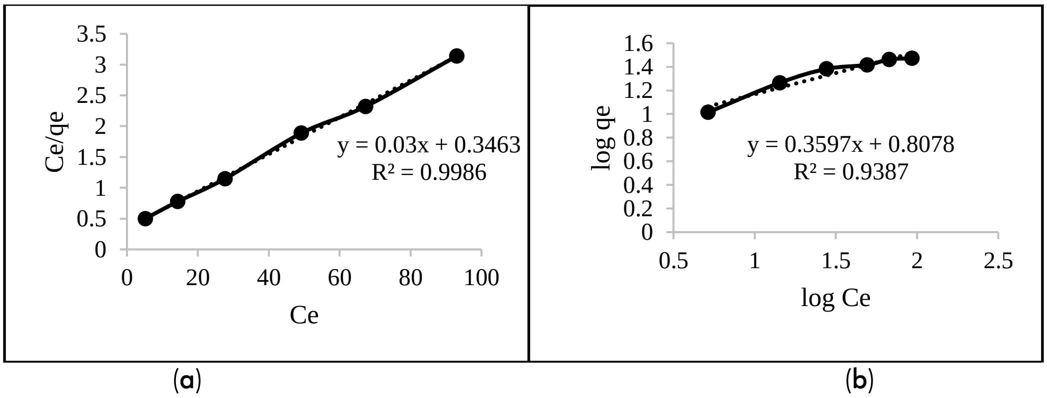

Figure 4. Langmuir model (**a**) and Freundlich model (**b**) of Congo red adsorption onto humic acid

Table 3. Equation data and correlation coefficient (R2) for Langmuir and Freundlich adsorption isotherms

Dyes	Langmuir			Freundlich	
	Linier	q (max) (mg/g)	R^2	Line equation	R^2
Congo red	y=0.03x+0.3463	33.33 mg/g	0.9986	y=0.3597x+0.8078	0.9387

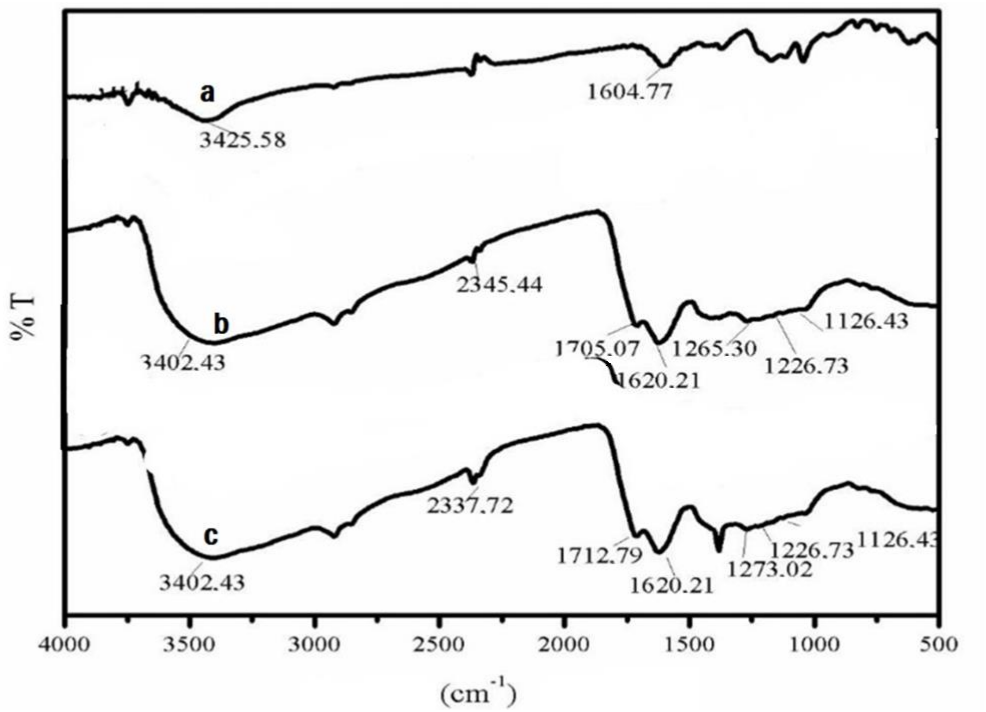

Figure 5. Spectra of Congo red (**a**), humic acid after adsorption (**b**), humic acid before adsorption (**c**)

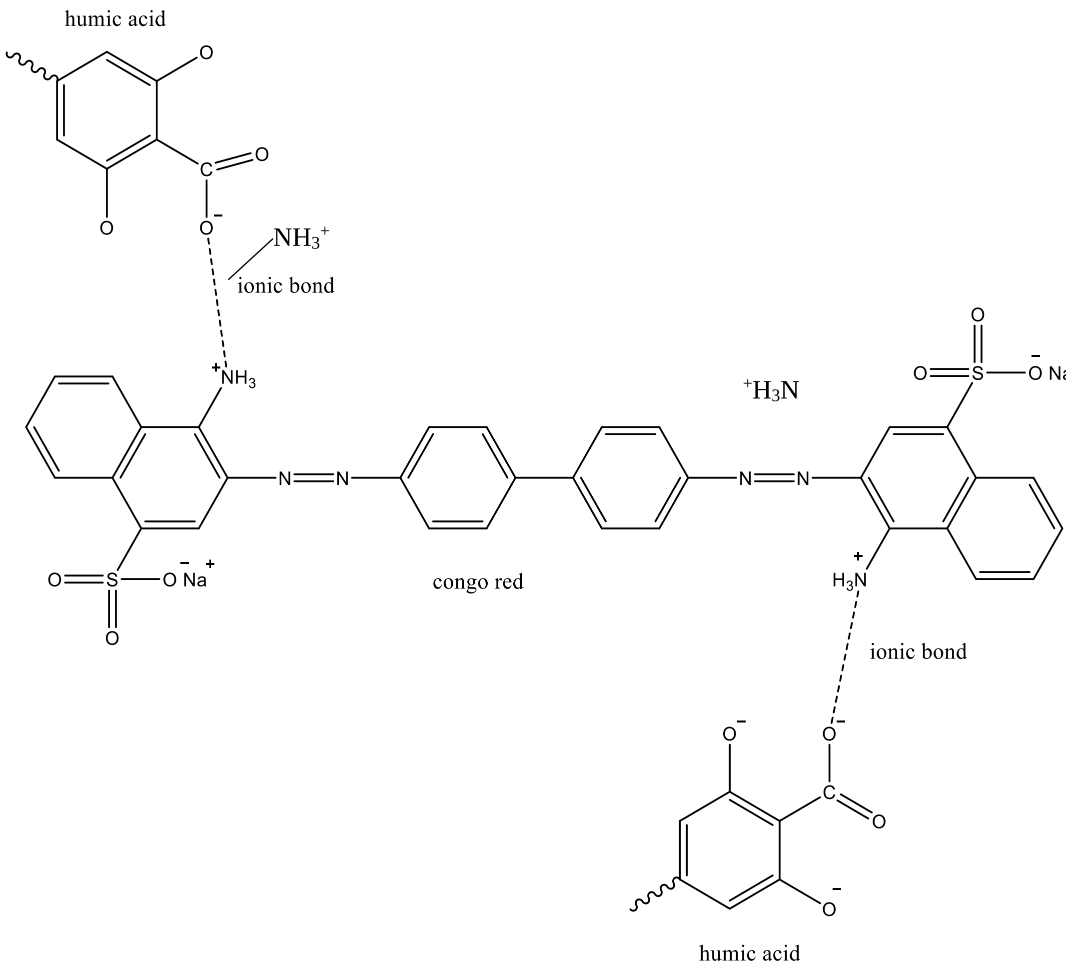

Figure 6. The prediction electrostatic interaction between Congo red and humic acid

This study used Langmuir model and Freundlich model (**Figure 4**) to determine the type adsorption of Congo red onto humic acid. Based on **Figure 4** and **Table 3**, Langmuir model was better fitted than Freundlich model with regression coefficient (R^2) 0.9926. Therefore, Congo red adsorption onto humic acid have been rightly explained by Langmuir adsorption isotherm model which is applies a single layer (monolayer) adsorption on the surface of a homogeneous substance and can only adsorb one molecule for each molecule of the adsorbent and there is no interaction between the adsorbed molecules. The monolayer adsorption capacity of Congo red onto humic acid of 33.33 mg/g. These results obtained are similar to the Congo red adsorption onto jute stick powder of 35.7 mg/g (Panda, 2009), sunflower stalk biomass of 34.26 mg/g (Shi, 1999). Thus, humic acid has the ability to adsorb anionic dyes, like Congo red.

Adsorbat onto Humic Acid Characterization

FTIR spectra of Congo red, humic acid before and after the adsorption of Congo red was showed in **Figure 5**. Before adsorption the broad band at 3,402.43 cm^{-1} (b) was ascribed to stretching vibration of -OH, 1,712.79, 1,620.21 and 1.273,02 cm^{-1} was ascribed to vibration of carbonyl C=O, C-O alcohol and aromatic C=C. After the adsorption the signal at 1,712.79 cm^{-1} were shifted to 1,705.07 and 1,273.02 cm^{-1} were shifted to 1,265.30 cm^{-1}. Therefore, shifting of the signal suggested the possible of interaction between Congo red and humic acid. The prediction electrostatic interaction between Congo red and humic acid is shown in **Figure 6**.

CONCLUSIONS

Based on this research, humic acid is an effective adsorbent for Congo red. The parameters pH, contact time, and adsorption capacity were studied. pH adsorption of Congo red onto humic acid occurs at pH 6 with a contact time of 120 minutes. The adsorption capacity of Congo red onto humic acid of 33.33 mg/g and follows the Langmuir model with R^2 = 0.9926.

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