Insertion of bentonite with Organometallic [Fe$_3$O(OOC$_6$H$_5$)$_6$(H$_2$O)$_3$(NO$_3$).nH$_2$O] as Adsorbent of Congo Red

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Abstract: The adsorption of Congo red using bentonite inserted organometallic has been investigated. The insertion bentonite was characterized using FT-IR Spectrophotometer, XRD and XRF analysis. The FT-IR characterization showed the higher intensity of peak wavenumber at 470.6 cm^{-1} for Fe$_3$O on the ratio 1:3. While the XRD characterization showed the shift of diffraction angle of 2θ was 5.2° and has a basal spacing of 16.8 Å. In the XRF characterization, the insertion process of organometallic occurred optimally with the percentage of metal oxide reached 71.75 %. The adsorption process of bentonite inserted organometallic compound [Fe$_3$O(OOC$_6$H$_5$)$_6$(H$_2$O)$_3$(NO$_3$)·nH$_2$O] showed the adsorption rate (k) is 0.050 min^{-1}, the largest adsorption capacity (b) at 70ºC is 4.48 mol/g, the largest adsorption energy at temperature 30ºC which is 6.4 kJ/mol Organometallic compounds. The value of the enthalpy (ΔH) and entropy (ΔS) decreased with increasing concentrations of the Congo red. Effect of pH on the adsorption on at pH 3 shows the biggest of number Congo red absorbed is 19.52 mg/L for insertion of bentonite.

Keywords: Bentonite, [Fe$_3$O(OOC$_6$H$_5$)$_6$(H$_2$O)$_3$(NO$_3$)·nH$_2$O], Congo red dye

1. Introduction

Organics pollutant such as coloured dye can be found industries effluent such as textiles, rubber, paper, plastic, cosmetics, etc. Discharging dyes into river although in a small amount can affect the organisme life. As dyes are designed resist with time and exposure to sunlight, they cannot be easily removed by conventional wastewater treatment. Thus, dye removal has been an important but challenging area of wastewater treatment. To remove dyes and other colored contaminants, the famous method used was adsoption [1].

Bentonite is a layered material or clay containing inorganic minerals found in nature [2]. Bentonite is used as an adsorbent [3]. Bentonite in its application as an adsorbent has deficiency among others containing impurities minerals so that its absorption is not optimal. Therefore, to optimize the absorption of bentonite activation needs to be done. The activation process aims to separate impurities naturally on bentonite. In the activation process, there are 2 ways done that are by physical way or chemical way.

In the physical process, combustion at high temperatures causes the removal of water molecules from the crystal sequence, so that two adjacent OH groups release one molecule of water [4], while in the chemical process using sulfuric acid aims to remove the metals of size small. This is due to the metals present in bentonite bound to the H^+ ions derived from the acid thus the layer acting as the insertion admission will be more open. Bentonite modification is expected to produce bentonite which has high adsorption ability and can perform insertion process that produces insulated atomic bentonite, molecule or complex compound.

Said and Palapa[5] found that the insertion process using Al_2O_3 metal oxide shows a slight increase in the distance between layers. This is indicated by the variation of contact time of adsorption of bentonite inserted metal oxide compound Al_2O_3 to ammonia at 4, 8, 16, 24 hours resulted that at 24 hours bentonite inserted Al_2O_3 able to adsorb ammonia with the largest percentage, while in an adsorption process, time 24 hours is so long that bentonite inserted Al_2O_3 metal oxide compounds can be said not yet optimally used as an adsorbent because of the size of the cation possessed by small metal Al_2O_3 oxide to become inserted bentonite.

Therefore, in this research, bentonite insertion process using organometallic compound as insertion will be done. The organometallic compounds $[Fe_3O(OOC_6H_5)_6(H_2O)_3(NO_3)\cdot nH_2O]$ have advantages such as high reactivity properties and larger cation size (macrocation). It is expected that bentonite insertion of organometallic compounds capable of inserting optimally and able to increase high adsorption capacity.

Bentonite inserted macrocation of organometallic compounds characterized using FT-IR, XRD, and XRF spectrophotometers to see the metal oxide composition. Further, bentonite inserted an organometallic compound to be used as an adsorbent to adsorb the Congo red dye. In this study, the selected adsorbate is Congo red dye, because this dye includes hazardous waste. The Congo red adsorption process that occurs can be affected by several conditions including the influence of adsorption time, the influence of concentration and temperature, and the pH of the solution. Determination of equilibrium concentration on the adsorption of activated bentonite and bentonite insertion of the organometallic compound was analyzed using UV-Vis spectrophotometer.

2. Materials and Method

2.1. Material
The materials used in this study are natural bentonite, Congo red dye, sulfuric acid, aquadest, iron (III) nitrate nonahydrate $[Fe(NO_3)_3.9H_2O]$, benzoic acid, Sodium hydroxide 0.1 M, and hydroxide acid 0.1 M. The characterization of bentonite was done with X-Ray spectroscopy Diffractometer (Shimadzu lab X-type 6000), FT-IR spectrophotometer (Shimadzu-Prestige-21), X-Ray fluorescence, PAN Analytical Type Minipod 4) and Uv-Vis spectrophotometer (Thermo Scientific Geneysis 20).

2.2. Bentonite inserted with Organometallic Compounds $[Fe_3O(OOC_6H_5)_6(H_2O)_3(NO_3)\cdot nH_2O]$
A total of 5 g of bentonite was dissolved in 200 mL of aquadest. A 15 g of the organometallic compound acting as the insertion compound is prepared by adding 100 mL of 1 M NaOH, then mixed in reflux and stirred vigorously for 24 hours at room temperature for 1 day while being fed by nitrogen gas. The resultant insertion of organometallic compounds is then washed with aquades and dried in open-air for 24 hours. The results of bentonite insertion of organometallic compounds were characterized using XRD, FTIR, and XRF spectroscopy.

2.3. Study of Adsorption of Congo Red

2.3.1. Effect of adsorption time
A total of 0.03 grams of bentonite adsorbent inserted organometallic compound and activated bentonite (control) were added to 50 mL Congo red with a concentration of 150 mg / L then stirred with a horizontal shaker at 30 min intervals. Variations in absorption time varied from 10, 20, 30, 40, 50, 60, 70, 80, and 90 min. Congo red which has gone through the adsorption process is silenced then measured its concentration by using Uv-Vis spectrophotometer to find out

2.3.2. *Effect of Concentration and Temperature*

The thermodynamic studies of dye adsorption on bentonite inserted macrocation adsorbents were carried out through a series of experiments by varying the concentration of dyestuff and adsorption temperature. A total of 0.03 g of adsorbent was mixed with 50 mL of 25, 50, 75, 100 and 150 (mg/L) dye solutions used as controls and for bentonite insertion of its organometallic compound using dye solutions of 10, 20, 30, 40 and 50 (mg/L), then stirred using a horizontal shaker for 1 hour at varying temperatures (30, 40, 50, 60, and 70°C). The solution was silenced and measured using a UV-Vis spectrophotometer to determine the residual concentration and dyestuff adsorbed concentration after adsorption.

2.3.3. *Effect of pH*

The effect of pH on dye adsorption on bentonite inserted organometallic compounds was studied by varying the initial pH of the dye solution. Adsorbent bentonite inserted as much as 0.03 grams was added to 50 mL dye solution at 25 mg / L concentration and then stirred with a horizontal shaker at room temperature for one hour. The initial pH of the dye solution is set at 3, 4, 5, 6, 8, 9, 10, 11, and 12 for inserted bentonite while for the activated bentonite (control) the initial pH of the dye solution is set to 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, and 12 were added with 0.1 M NaOH addition and 0.1 M HCl of solution was allowed to stand for 10 min and measured using UV-Vis spectrophotometer to determine residual concentration and adsorbed concentration of the substance Color after the adsorption process.

2.3.4. *Congo red Interaction Studies*

The interaction between the adsorbent and the adsorbate is studied spectroscopically by looking at changes occurring in the adsorbent before and after the adsorption process. As much as 0.03 g of adsorbent bentonite insertion of the organometallic compound was mixed with 50 mL of dye with concentration 50 mg/L. The mixture is stirred using a horizontal shaker for 1 hour, then the mixture is separated through the filtration process. The adsorbents are then dried with an oven at 80°C. Adsorbents that have been used for the adsorption process are then analyzed using FT-IR to determine the functional group changes occurring before and after the adsorption process.

2.4. *Data Analysis*

The adsorption process is studied through kinetic and thermodynamic parameters. The adsorption kinetic is studied by variation of adsorption time and adsorption rate calculated based on Langmuir-Hinnshelwood adsorption equation as follows:

$$\frac{\ln(\frac{C_0}{C})}{C} = k_1\frac{t}{C} + K \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \qquad (1)$$

where:

C_0 = the initial concentrations
K_1 = the rate of adsorption
C = Concentrate Congo red after time
t = Adsorption time
K = Adsorption equilibrium constant

The thermodynamic parameters studied through variations in the concentration of Congo red dye, adsorption capacity and adsorption energy were calculated on the basis of the Langmuir equation as follows:

$$\frac{C}{m} = \frac{1}{bK} + \frac{C}{b} \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \qquad (2)$$

$$E = - RT \ln K \qquad \text{..} \qquad (3)$$

where:

C = The concentration of Congo red after adsorption reaches equilibrium
m   = Mol Congo red adsorbed
K   = Equilibrium constant
b   = Adsorption Capacity
E   = Adsorption Energy
R   = Constanta
T   = Temperature

While to find the value of coefficient of adsorbate distribution used equation as follows:

$$\ln Kd = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad \text{...} \qquad (4)$$

.where:

Kd = Coefficient of adsorbate distribution (qe/Ce)
ΔH = Entalphi
ΔS = Entrophi
R   = Constanta
T   = Temperature

3. Results and Discussion

3.1. Effect of Adsorption Time

The adsorption time calculation data on the amount of adsorbed Congo red can be seen in Figure 1.
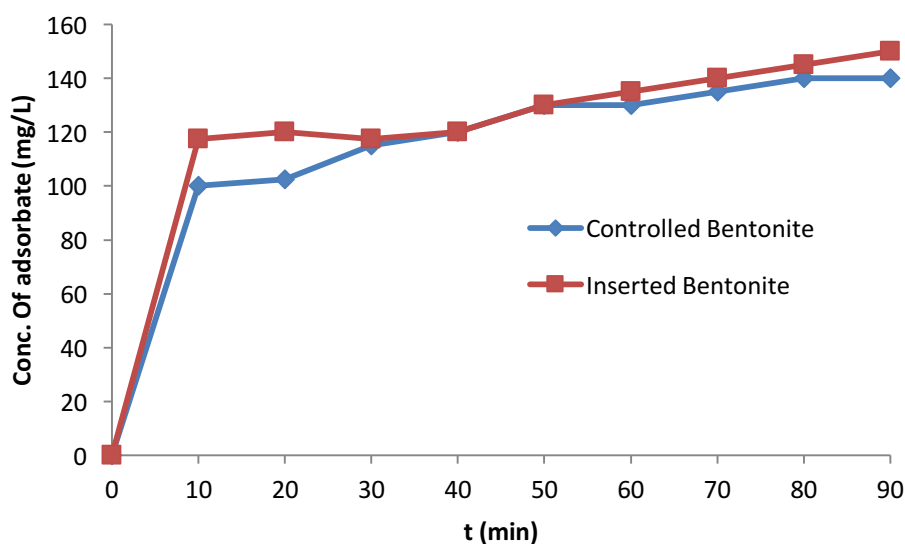

Figure 1. Influence of contact time of activated bentonite (control) and inserted bentonite to the amount of adsorbed Congo red

Figure 1 shows as the adsorption time increase, the greater the concentration of the adsorbed Congo red dye. In bentonite inserted to see the amount of the adsorbed red dye Congo increase within 20 minutes as it reaches the equilibrium time. This shows that bentonite inserted organometallic

compound has reached the adsorption equilibrium. Adsorption time data can be used to determine the kinetic parameters calculation adsorption. Data of kinetic parameters presented in Figure 2 and b.

Based on the Langmuir-Hinshelwood equation, the adsorption constant rate can be calculated as the slope of the ln (Co/C)/C plot to t/C as the line equation. The value of each slope as the rate of adsorption constant (k1) and the correlation coefficient (R^2) of the plot (Co/C)/C to t/C is presented in Table1. The correlation coefficient obtained shows linear line equation. The equation of the line with the correlation coefficient (> 0.9) shows that the Congo adsorption kinetics credits the Langmuir-Hinshelwoodoold kinetics equation.
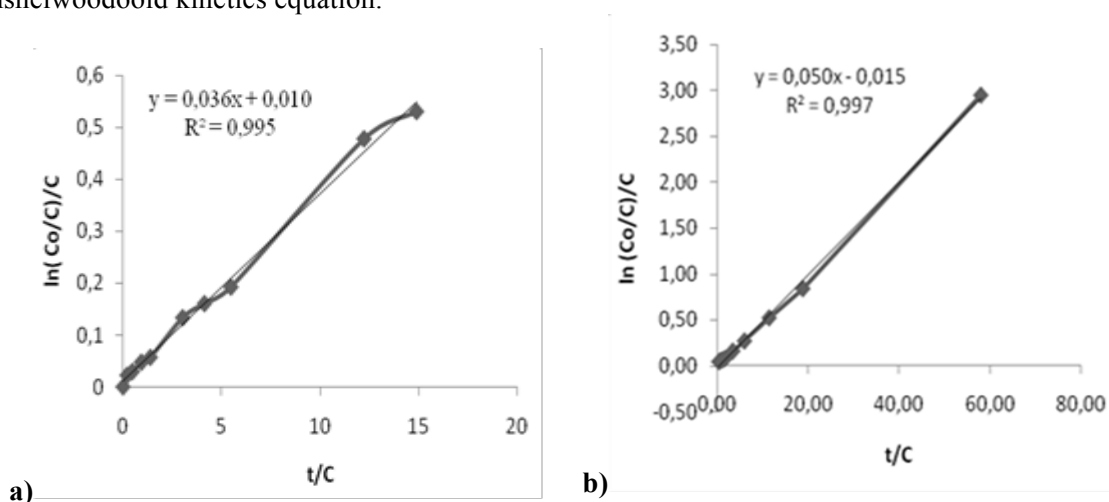

Figure 2. The bentonite adsorption kinetic parameters: a) controlled, and b) inserted bentonite

Table 1. Values of adsorption rates for Activated Bentonite (control) and Inserted Bentonite

Adsorbent	Rate of adsorption (min^{-1})	R^2
Activateded bentonite	0.036	0.995
Inserted bentonite	0.050	0.997

It is shown that the activated bentonite have the good ability as adsorbents. This is based on the basal spacing between the activation and inserted bentonite. From the previous study [6], It is found that the activated bentonite at 2 per angle shift has basal spacing 24 Å while inserted bentonite has basal spacing of 16,8 Å. The difference of basal spacing has only a slight gap. The more differences between them happened because of the adsorbate enter to inserted bentonite layer by layer. Solute attaches to the surface of montmorillonite and diffuses into the pores before finally being trapped inside of the adsorbent. The solute will be continuously deposited on the surface of the adsorbent and the layer will become thicker. The interaction force, between the solute and the adsorbent, means that the solutes cannot leave the adsorbent [7]. It is also known that the montmorillonite crystal structure consists of three layers: two units of the tetrahedral layer and one octahedral layer [8]. It can be said that the inserted bentonite rate of adsorption is higher than the activated one.

3.2. Effect of Concentration and Temperature

The curve of adsorption as the effect of concentration and temperature on the amount of adsorbed Congo red was presented in Figure 3a and b. The figures show the influence of temperature and concentration on the adsoprtion process of Congo red. It can be seen from the figure that the activated bentonite show the better performance than the inserted bentonite with it marked by the higher value of adsorbate concentration. This phenomenon was explained by another researcher[9,10]. The Congo red color has a S = O vibration with a very low intensity at 1072 cm^{-1} wave numbers. In addition, the aromatic C = C vibration appears at 1481 cm^{-1} wave numbers. The symmetric stretching vibration of the organometallic compound will reduced before the adsorption[9]. In addition, the adsoprtion capacity decreased with the increasing concentration. It is found that the higher temperature is to the

advantage of adsorption and that the adsorption is an endothermic reaction. It is well known that increasing temperature may produce a swelling effect within the internal structure of absorbent, penetrating the large dye molecule also will block the pore of adsorbent. Finally, it will reduce the adsorbent performance[10].
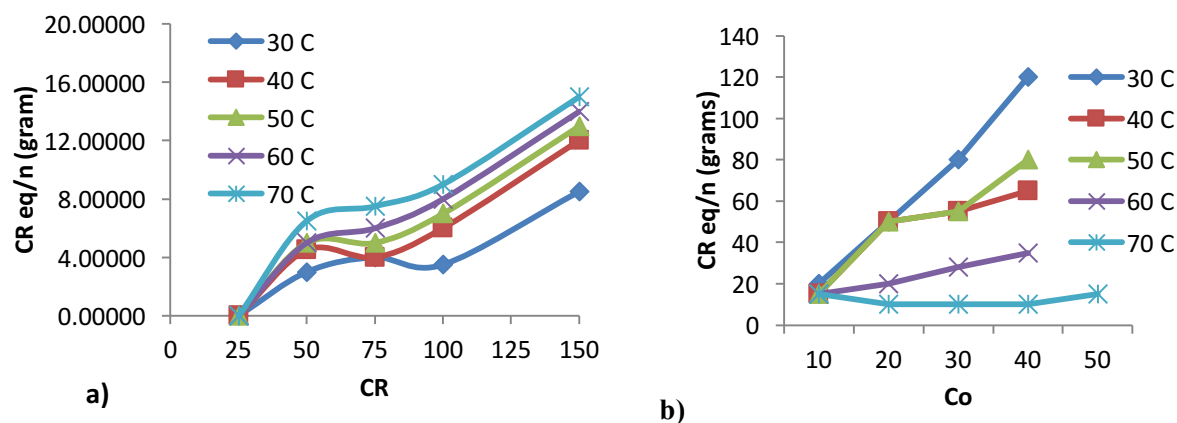

Figure 3. Effect of adsorption temperature and concentration: a) activated, and b) inserted bentonite

In addition, Figure 3 shows the number of Congo red adsorbed by activated bentonite greater than the inserted bentonite. This is due to the activated bentonite has a spacing between layers very small so when the adsorbate, Congo red directly entry to the inside of adsorbent, it is more easily filled compared to the inserted bentonite that has a greater spacing between layers. It can be concluded the activated bentonite is more reactive than inserted bentonite [11]. Furthermore, we calculate the kinetic and thermodinamic parameters using the equation 2,3 and 4. The result of kinetic parameter such as adsoprtion capacity and energy of adsorption are list in Table 2 while the thermodynamic parameters such as changes in Gibbs ($\Delta G°$), enthalpy ($\Delta H°$) Entropy ($\Delta S°$) are list in Table 3.

Table 2. The kinetic parameter of adsorption process of activated and inserted bentonite

Adsorbent	Activated bentonite					Inserted bentonite				
Temp. (c)	30	40	50	60	70	30	40	50	60	70
b (mg/g)	15.6	43.4	71.4	62.5	58.8	0.35	0.59	0.72	1.33	4.48
E (kJ/mol)	-7.64	-5.32	2.21	7.02	10.9	-6.4	-3.83	-4.22	-1.93	-0.08

Table 3. The thermodynamic parameter of adsorption process of activated and inserted bentonite

Adsorbent	Activated bentonite					Inserted bentonite				
Conc. (ppm)	25	50	75	100	150	10	20	30	40	50
ΔH (kJ/mol)	69.5	81.8	59.1	54.6	42.2	59.4	153.2	190.2	198.3	124.2
ΔS (kJ/mol)	0.256	0.292	0.215	0.2	0.155	0.109	0.263	0.325	0.336	0.212

The adsorption capacity (b) of the activated bentonite (control) increased from 30 to 50°C but at 60 and 70°C, the adsorption capacity decreased. The inverted results was found to the inserted bentonite, the capacity of adsorption (b) has improved very well as temperature increases. This shows that in bentonite activated its optimum adsorption capacity at 50°C. For the adsorption energy, it is seen that the temperature of 70°C has the highest energy of adsorption. Further, the highest enthalphy and entropy occurs in inserted bentonite with Congo red concentration of 40 mg/L were 198.3 kJ/mol and

0.336 kJ/mol, respectively. This happens because adsorbent adsorbate irregularly occurs on the surface only and into the surface, it appears that even though the energy is large but the adsorption capacity is not so great and vice versa if the energy is small but it has a large amount of capacity.

3.3. Effect of pH
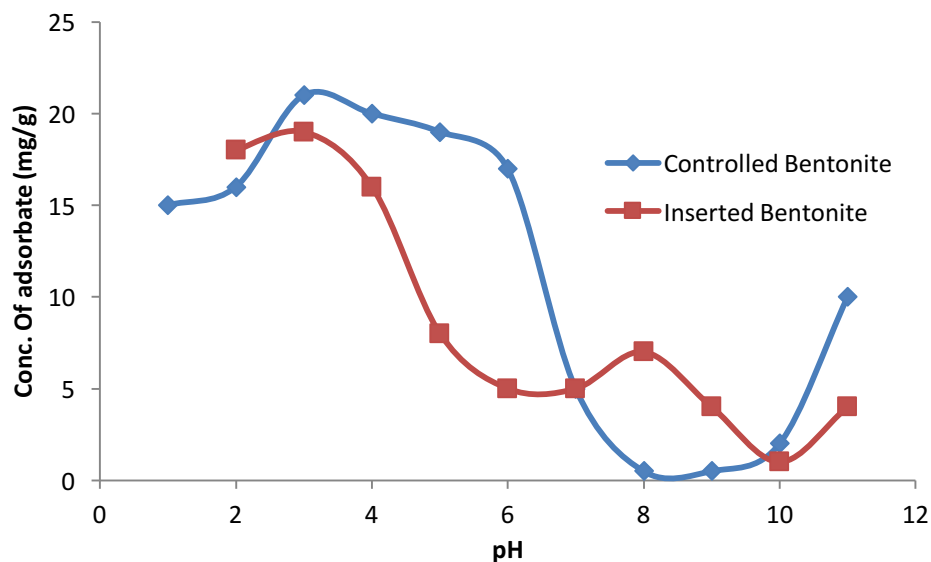Effect of pH on the adsorption of Congo red dye is showed in Figure 4.

Figure 4. Effect of activated bentonite adsorption pH (control) and bentonite insertion of organometallic compound to the amount of Congo red adsorbed

The Congo red dye adsorption process by activated bentonite (control) has an initial pH of 4. After added the hydrochloric acid (HCl), the pH reached 3 and consequently the number of Congo red adsorbed was increased. In vice versa, after pH reahed 2 and 1, there was a decrease in the amount of adsorbed (Congo red). In the inverted process by adding process the sodium hydroxide (NaOH), the reducing number of Congo red was existed. However, in the of addition of sodium hydroxide (NaOH) so that the pH reaches 6 there is a decrease in the amount of adsorbed red Congo characterized by a concentration of Congo red dyestuff adsorbed by bentonite inserted into dark red. Two possible mechanisms of adsorption of Congo red may be considered: (a) electrostatic interaction between the protonated groups of bentonite and the dye, and (b) the chemical reaction between the adsorbate and the adsorbent [12].

　　As the pH was 8, the concentration of adsorbate adsorbed rises again. This is because of the more the addition of NaOH the more the amount of adsorbate is adsorbed and the solution is marked to be pink. Similarly, activated bentonite, Congo red adsorption by the adsorbent inserted bentonite organometallic compounds also showed a decrease in the amount of Congo red adsorbed at pH 8, 9, 10 followed by changes in the blend color to red tea. The existence of Congo red discoloration on adsorbed by the activated and inserted bentonite either in acidic or alkaline conditions based on pH of Congo red dye which naturally has effective pH values in the range 3-6. When the atmosphere is a mixture acid solution then changes color to purple, whereas under alkaline conditions the mixture becomes colorless Congo red.

3.4. Interaction Studies of Activated and Inserted Bentonite with Organometallic Compounds using FT-IR
The gradual changes occur in the vibrational frequency associated with a specific chemical bond. It concerning the peak position shift of IR spectra are based on the notion that the extent of frequency shift can be directly correlated with the level of specific molecular interactions, such as hydrogen

bonding and dipole–dipole interactions. This also applies to the Congo red adsorption interaction study by activated and inserted adsorbent during before and after adsorption. Factors that affect the vibrational IR are acid activation, inserted organometallic and adsorption of congo red dye stuff process. During the acid activation process, the acid attack protons penetrate into the clay mineral layers and attack the structural OH groups[13]. By modification of bentonite through insertion of organo metallic will cause the basal spacing larger and consequently the adsorption capacity to increase. The existance of organometallic can be proven from shifting in IR spectra [14]. The vibration of the functional groups present in the Congo red dye will appear on the FT-IR spectrum with a typical wave number. The FTIR spectra before and after the activated bentonite adsorb Congo red dye contained was presented in Figure 5, while the spectra of inserted bentonite before and after Congo red dye adsorption was presented in Figure 6.
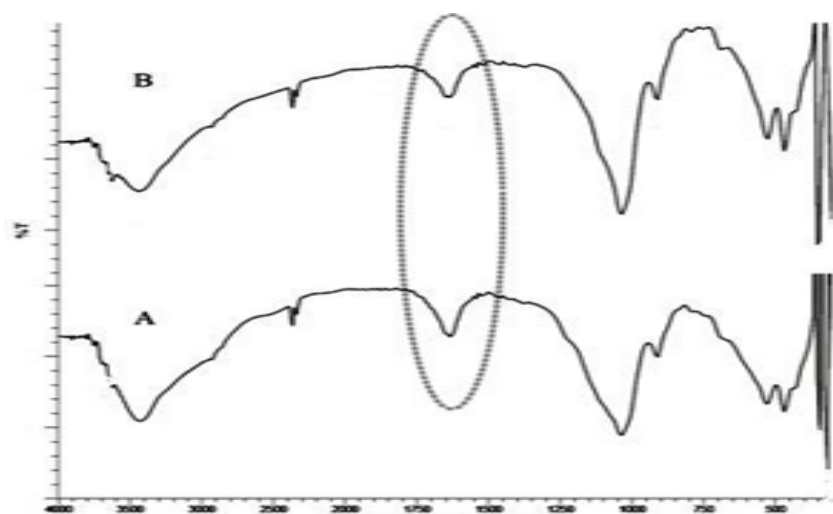

Figure 5. FTIR spectra of activated bentonite: a) before, and b) after adsorb the Congo red dye

Figure 5 shows the activated FT-IR bentonite spectrum changes before and after adsorb the non-contrasting Congo red substance. However, when viewed from the number of waves there is a difference of each bonding vibration. In the wave number 1041.5 cm^{-1} shows the vibration of Si-O-Si strain on bentonite and S = O of the Congo red dye with high intensity and sharpness. In addition, the bonding vibrations of bentonite after adsorbing Congo red appearing at the wave number 1635 cm^{-1} denotes the N=N vibration for the Congo red as a sign that the Congo red dye is an azo group.

Vibration NH contained in Congo red regional group appears at wave number 3618.4 cm^{-1}[15]. Figure 6 shows the change in the spectrum FT-IR bentonite inserts an organometallic compound before and after adsorb the visible Congo red dye. On the spectrum of inserted bentonite that have to adsorb dye Congo red visible vibration new bond indicates the group functional Congo red, which is the wave number 1635.6 cm^{-1}, which shows the absorption band for N=N as a marker of group azo.
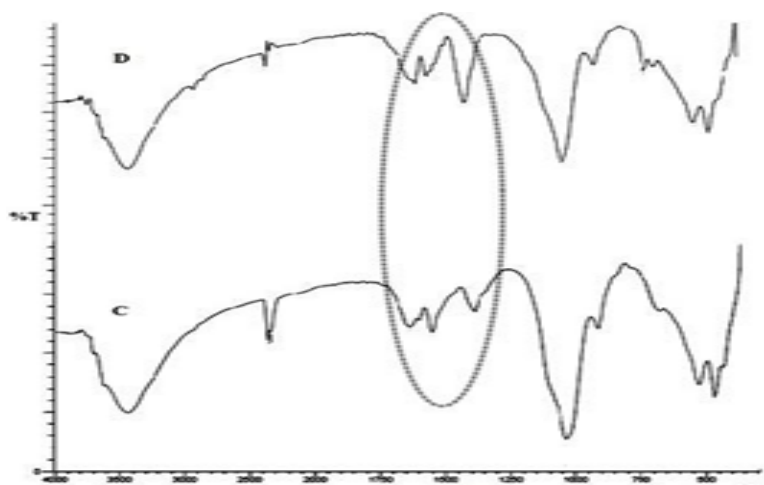
Figure 6. FTIR spectra of inserted bentonite: c) before, and d) after adsorb Congo red dye

4. Conclusion

The activated bentonite has smaller adsorption rate than the inserted bentonite i.e. 0.036 min^{-1} and 0.050 min^{-1}, respectively. The adsorption capacity of activated bentonite is greater than the inserted bentonite adsorbent as temperature increases. The greatest adsorption energy of activated bentonite was 11 kJ/mol at 60°C, while inserted bentonite was 6.4 kJ/mol at 30°C. The enthalpy of activated and inserted bentonite decreased with increasing the Congo red concentration. The lowest entropy was occured at 50 mg/L by activated bentonite of 0.155 kJ/mol, whereas in the lowest entropy of inserted bentonite was occured 0.109 kJ/mol at Congo red concentration of 10 mg/L. At pH 3 there was an increase in the amount of Congo red adsorbed by activated bentonite and inserted bentonite i.e. 20.45 mg/L and 19.52 mg/L, respectively.

Acknowledgment

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