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ADSORPTION OF CONGO RED USING KAOLINITE-CELLULOSE ADSORBENT

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ABSTRACT
Kaolinite was impregnated with cellulose extracted from rubber wood fibers has been done. The product of impregnated kaolinite-cellulose was characterized using FT-IR spectrophotometer. Furthermore, the impregnation results are used as an adsorbent of Congo red. Adsorption of Congo red was also studied the kinetic and thermodynamic parameters. The results of characterization using FT-IR spectrophotometer shows the process of impregnation was successfully conducted. It was indicated that the presence wavenumber at 910.4 - 918.12 cm^{-1} and 1033.85 cm^{-1} become 1026.13 cm^{-1} and the existence of vibration at wavenumber 2931.8 cm^{-1}. The pH of adsorption was adjusted to 4 before the adsorption process. The adsorption process of cellulose impregnated kaolinite shows the rate of adsorption (k) of 0.002 min^{-1}, the adsorption reviews largest capacity (b) at 50 ˚C was 500 mol/g. The greatest adsorption energy (E) at 40 °C is 11:09 kJ/mol. The enthalpy value (ΔH) and entropy (ΔS) decreased with increasing Congo red dye concentration.

Keywords: kaolinite, cellulose, impregnation, Congo red

INTRODUCTION

Clay is a material that consists of mineral rich in alumina, silica, and water. Clay mineral is layered silicate and commonly found in nature. One example of a layered material or clay is widely known that kaolinite (Deng, et.al, 2017). The chemical formula of pure kaolinite is aluminum silicate hydrate ($Al_2O_3.2SiO_2.2H_2O$). The minerals include kaolinite group is kaolinite, nacrite, and halloysite, with its main mineral kaolinite (Kovács and Makó, 2016).

In recent years, kaolinite has become the materials used for several of industrial processes due to its excellent performance like good bonding ability, a good electrical insulator, and thermal stability. However, it is rarely used as an adsorbent for the low cations exchange capacity and a small specific surface area (Koteja and Matusik, 2015). Crystal structure of kaolinite is classified to the type phyllosilicates 1: 1. This crystal consists of sheets octahedral aluminum, Al^{3+} coordinated to the anion OH^- stacked sheets of silica tetrahedral, Si^{4+} coordinated to the anion O^{2-} (Yu, et.al, 2016).

As an inorganic polymer, kaolinite minerals classified as inorganic ion exchangers who can naturally perform the exchange process with other ions from the outside with the influence of water (Chemeda, et.al, 2015). The clay structure is negatively charged and binding of cations to neutralize the charge. The negative charge is derived from the ratio between silica and alumina (Si/Al) which is relatively small and the surface of the kaolinite that has oxygen and hydroxyl groups sticking out, causing the negatively charged (Pietzsch et.al, 2015).

One of effort to improve the absorption of kaolin as an adsorbent can be modified by impregnation method. The impregnation is a process in which an adsorbent material that coats so that the active group of the material is also capable of binding the compound to be absorbed (Aung et.al, 2015). Impregnation technique can be done with certain organic materials and the process is easy and simple. Organic materials that can be used to modify the clay are cellulose, cellulose used because its existence is abundant in nature. Judging from the structure of cellulose has a huge potential to be used as adsorbent, because the -OH group that is bound to interact with the adsorbate. The presence of the -OH group in cellulose cause the polar properties on the adsorbent. Thus stronger cellulose absorbs substances that are polar substances that are less polar (Han et.al, 2016).

Studies of impregnation method have been carried out by Unuabonah et.al (2007) that has impregnated tripolyphosphate to kaolinite for adsorption of lead and cadmium. Chong et.al (2009) also reported impregnation of kaolinite using titania compound as material for photocatalyst.

The dye used in the apparel industry, paper, plastic, rubber, food and cosmetics to produce a colored product. The dye usually has a complex molecular structure which makes it more stable aromatic so difficult to disentangle biodegradable. Congo red is a dye that has an azo group (R - N = N - R). As the waste dye, where the dye Congo red, especially in the aquatic environment can damage a variety of species of life because of the nature of dye Congo red, which has a fairly high level of toxicity. If the dye Congo red accumulates in the human body can cause several health problems in humans (Sasmal et.al, 2017). Treatment and removal of Congo red from aqueous solution has been conducted by many researchers such as Said and Palapa (2017), which has Mg/Al hydrotalcite as material for adsorption of Congo red.

Concern on the effects of the textile dye Congo red on the environment and living beings in it, there should be efforts to minimize waste of the substance before being discharged into the water system. It requires an adsorbent that is able to absorb the dye better. Kaolinite impregnated cellulose is expected to be used as an adsorbent with a higher adsorption capacity, especially for organic molecules.

EXPERIMENTAL SECTION

Materials and Equipments

The materials used in this study are rubber wood fibers, kaolinite ($Al_2O_3.2SiO_2.2H_2O$), substance color Congo red ($C_{32}H_{22}N$-

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$_6Na_2O_6S_{2)}$, thiourea ($(NH_2)_2CS$) and sulfuric acid ($H_2SO_{4)}$, sodium hydroxide (NaOH), hydrochloric acid (HCl), and distilled water (H_2O). The tools used in this research that flask glassware, analytical balance, furnace, magnetic stirrer, thermometer, bath (hotplate), oven, horizontal shaker, filter paper, pipette volume, pipette, cuvette, spectrophotometers Shimadzu FT-IR-Prestige-21, and UV-Vis spectrophotometer Thermo Scientific Geneysis 20.

Preparation Rubber Wood Fiber

A 100 g of rubber wood fibers was washed using hydrochloric acid (HCl 0.1 M) with a certain volume for 3 hours while shaked. Washing results then filtered, and the solids obtained were washed with water and followed by washing using 0.1 M NaOH with a certain volume for 3 hours while shaked. Results immersion then filtered, and the solids obtained were washed with water until the washing water has a neutral pH. Then the solids are dried and the obtained results in the form of cellulose 1x washing characterized using FT-IR spectrophotometer. The characterization results compared to standard cellulose. The procedure is repeated from the beginning to get the cellulose 2x, 3x, and 4x wash.

Determination of Water Content

The water content is determined by measuring the sample weight measurements before and after heating. A total of 1 g of rubber wood fibers incorporated into a petri dish of known weight. The wood fiber was heated in an oven at 110 ˚C for 5 hours, then allowed to stand and weighed. This procedure applies to launder 2x, 3x, and 4x to obtain a constant weight.

Determination of Ash Content

The ash content is determined by incorporating 1 g of wood fiber (washed) in exchange porcelain that has been known weight. The wood fiber is heated into the furnace at a temperature of 400 ˚C for 2 hours to form ash, then allowed to stand and weighed. The procedure applies to launder 2x, 3x, and 4x to obtain cash heavy.

Preparation and Activation Kaolinite

Preparation kaolinite is done by two types i.e. physical and chemical activation. For physical activation, a 100 g of kaolinite was heated using the furnace at a temperature of 400 ˚C for 2 hours and then allowed to stand at room temperature. The Kaolinite was named heated Kaolinite. The other kaolinite was processed by chemical/acidification process. Acidification is done by dissolving 20 g of kaolinite which has been heated at a temperature of 400 ˚C into 200 ml of sulfuric acid ($H_2SO_{4)}$ the concentration of each 1%, 5%, 10%, and 15% in the beaker glass separately and stirred for 3 hours. Once separated and filtered, then each dried solid at a temperature of 97 °C. Further kaolinite which has been prepared called acidified kaolinite. Natural kaolinite, heated kaolinite, and acidified kaolinite were characterized by using FT-IR spectrophotometer.

Impregnation Kaolinite with Cellulose

Impregnation process carried out as follow. Kaolinite solids-cellulose was prepared by adding 4 g of cellulose from wood fiber rubber into a mixture of 1.5 M NaOH solution and the solution of thiourea 1 M. The mixture was stored at 0 ˚C for 8 hours to obtain a solution (I). A 10 g of activated kaolinite mixed with NaOH 46% as much as 8 mL in ice water for 6 hours. A 52 g of ice was added to obtain a solution (II). The solution (I) and (II) are mixed and stirred for 30 minutes to obtain a solid, and then filtered. The solid is filtered drip with sulfuric acid (H_2SO_4) 5% solids obtained are then dried and the impregnation result kaolinite-cellulose. Results of kaolinite-cellulose impregnation characterized using FT-IR spectrophotometer.

Applications of Cellulose Fibers Rubber Wood (Control), Activated Kaolinite and Kaolinite Impregnated Cellulose as Dye Adsorbent Congo Red

Preparation of standard solution of Congo red

Preparation of standard solution of dye Congo red made by diluting the mother liquor dye Congo red 1000 mg/L is used as a concentration of 10, 20, 30, 40 mg/L gradually. Standard solution of dye Congo red the adsorption by the adsorbent for the process of cellulose from wood fiber gum, kaolinite and kaolinite activated impregnated cellulose. Furthermore, each standard solution concentration Congo red measured wavelength of maximum absorbance at 503 nm using Uv-Vis spectrophotometer. Having obtained the equation absorbance then made a straight line with the x-axis dye concentration Congo red on the y-axis as absorbance.

Influence of Time Adsorption

A 0.03 g of each adsorbent is added to 50 mL Congo red with a concentration of 40 mg/L in a separate flask. The adsorbent was stirred with a horizontal shaker at predetermined intervals. The variation of the adsorption time starts at 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 minutes. Congo red that has gone through the adsorption process is separated and the absorbance was measured using a UV-Vis spectrophotometer. The amount of residual concentrations (mg/L), the amount of dye Congo red adsorbed (mg/L) was calculated using the equation of the calibration curve standard solution, while the rate of adsorption ($k_{1)}$ can be calculated using the Langmuir equation as shown in formula 1.

Influence of Temperature and Concentration of Congo red

Effect thermodynamics Congo red dye adsorption by cellulose (control), kaolinite activated (control) and kaolinite impregnated cellulose is done through a series of experiments with varying concentrations of dye Congo red adsorption and temperature. A total of 0.03 g adsorbent cellulose (control) and kaolinite activated (control) were mixed with 50 mL of dye Congo red (5, 10, 15, 20, 25 mg / L), and as much as 0.03 g kaolinite adsorbent impregnated cellulose mixed with 50 mL of dye Congo red (10, 20, 30, 40 mg / L). The adsorbent which has been mixed with dye Congo red is stirred using a horizontal shaker for 30 minutes at varying temperatures (30, 40, 50, 60 and 70 ˚C). The mixture is separated, then a solution of dye Congo red that has separated from the adsorbent measured absorbance values using a UV-Vis spectrophotometer to determine the concentration of residual dye Congo red after the adsorption process. The adsorption capacity (b), the adsorption energy (E) can be calculated using the Langmuir equation in formula 2 and 3, while the adsorption enthalpy (ΔH), and the adsorption entropy (ΔS) can be calculated using formula 4.

Data Analysis

The success of kaolinite with cellulose impregnation process was observed from FT-IR spectrum. Impregnation process optimal expected to form the adsorbent can be applied to the process of adsorption of the dye Congo red to see the parameters of kinetic and thermodynamic

Data kinetics of cellulose (control), kaolinite activated (control), and kaolinite impregnated cellulose is used to determine the rate of adsorption ($k_{1)}$ assuming that the adsorption process that occurs following the model of the Langmuir adsorption equation as

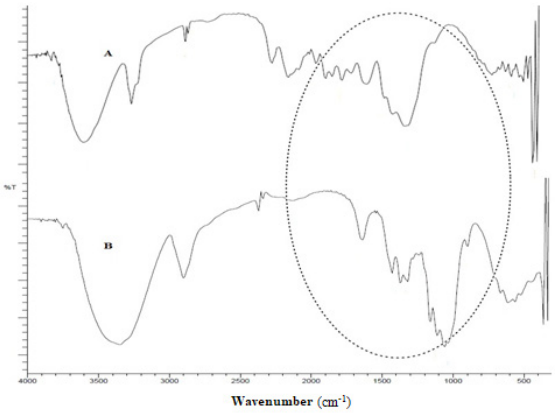

Figure 1. FT-IR spectrum of (A) the separation of cellulose wood fibers rubber (B) standard cellulose

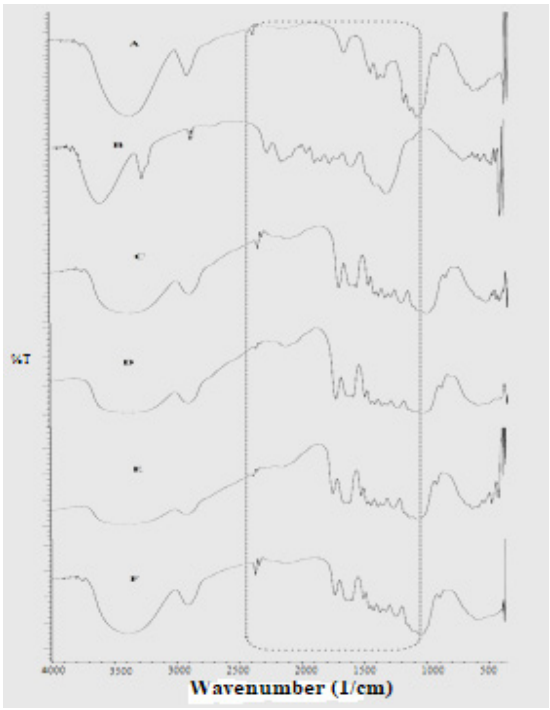

Figure 2. FT-IR spectrum of (A) standard cellulose; (B) the separation of the cellulose fibers rubber wood; cellulose washery 1x (C); 2x (D); 3x (E); 4x (F)

follows:

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

Where:

C_0 = initial concentration of Congo red (mg/L)
C = concentration of residual Congo red (mg/L)
t = adsorption time (min)
k_1 = rate of adsorption (min^{-1})
K = constant adsorption equilibrium

Thermodynamic parameters of cellulose impregnated kaolinite adsorption processes such as adsorption capacity and adsorption energy can be determined using the Langmuir equation as follows:

$$C/m = 1/bK + c/b \quad (2)$$

$$E - RT \ln K \quad (3)$$

Where:

C = concentration of residual Congo red (mg/L)
m = mol of Congo red adsorbed on kaolinite
K = equilibrium constant
b = adsorption capacity (mol/g)
E = energy adsorption (kJ/mol)
R = constant
T = temperature

while to find the value of the distribution coefficient of adsorbate used the following equation:

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

Description:

K_d = distribution coefficient of adsorbate *(qe*/Ce)
ΔH = enthalpy
ΔS = entropy
R = constant
T = temperature

RESULTS AND DISCUSSION

Identification and Characterization of Cellulose Results Separation of Wood Fiber Rubber using Spectrophotometer FT-IR

Fiber rubber wood taken from wood processing waste already separated, so that the residue obtained in the form of a mixture of cellulose, lignin and hemicellulose. Cellulose result of separation of rubber wood fibers identified using FT-IR spectrophotometer is then compared with the FT-IR spectrum of standard cellulose as presented in Figure 1.

In Figure 1 looks FT-IR spectra of standard cellulose showed absorption at wavenumbers 3348.42 cm^{-1} which is the stretching vibration of the hydroxyl group (OH). Wavenumber in 2900.94 cm^{-1} indicates -CH vibration which is a constituent group of the cellulose structure and reinforced with vibration at wave number 1427.32 cm^{-1} and 1373.32 $cm^{-1.}$ CO group which is a carbon chain connecting the cellulose compound is located in the fingerprint region at wavenumber 1250-1030 cm^{-1} and a stretching vibration.

FT-IR spectra of the cellulose separation results show similarities with the standard cellulose, which in the area of 3410.15 cm^{-1} the hydroxyl (OH), -CH group at wavenumber 2924.09 cm^{-1} and reinforced with vibration on wavenumber 1427.32 $cm^{-1,}$ 1373.32 cm^{-1} and 1327.03 cm^{-1} i.e. in the fingerprint region 1250-1050 cm^{-1} indicate the presence of ether groups (-CO). In the IR spectra of cellulose from wood fiber rubber looks still their unwanted vibration that is at wave number 1600 - 1700 cm^{-1} that indicates aromatic compounds making up the structure of lignocellulose. Therefore, necessary separation process can be continued in order in pure cellulose.

Cellulose separation of compounds undesirable done by soaking the back of cellulose using hydrochloric acid at a concentration of 0.1 M for three hours while stirring followed by immersion using sodium hydroxide at a concentration of 0.1 M with stirring for three hours. Soaking using HCl intended to break the hemicellulose and lignocellulose while NaOH solution is used to dissolve the lignin, hemicellulose and other compounds in order to get pure cellulose (Taflick et.al, 2017). Soaking using HCl and NaOH are repeated four times in order to obtain increasingly pure cellulose.

Table 1. The moisture content and ash content of cellulose from wood fiber washing

Washing	Water Content (%w/w)	Ash content (%w/w)
1	6.52	6.86
2	4.85	6.73
3	3.96	6.00
4	1.98	0.92

Cellulose separation results are identified using a spectrophotometer FT-IR and spectra are then compared to standard cellulose.

Figure 2 show that the FT-IR spectrum of cellulose results 4x laundering has similarities with the standard cellulose IR spectra. Especially in the area of 2368.59 cm wave number^{-1} where the FT-IR spectra of cellulose results showed absorption 4x laundering sharp and strong intensity in the region of the wave numbers compared to the FT-IR spectra of cellulose washery 1x, 2x and 3x. In the 1100-1600 cm^{-1}, the absorption area for laundering proceeds 4x cellulose has similarities with FT-IR spectra showing the vibration standard cellulose -CH group.

Characterization of Wood Fibers Cellulose Rubber Results Washing through Content Determination of Water and Ash Content. Result of the determination content of moisture and ash content of cellulose from wood fiber rubber washing results are presented in Table 1.

Water content like presented in Table 1 shows the water can be removed by heating at a temperature of 100-110 ˚C. Determination of the water content of an adsorbent conducted to determine the hygroscopic properties of the adsorbent because of high water in the adsorbent will reduce his ability as adsorbent due to pores are filled molecules of H_2O (Sharma et.al, 2017). In general, the desired moisture content has a low water content. It also deals with Waku save fuel to be used which in this case is cellulose from wood fiber rubber washing results. If the high water content in the storage cellulose cannot be done in the long term and its use will be limited. In this study, cellulose from wood fiber washing results 4x repetition has the smallest water content. In the first washing, the cellulose has a water content by 6.52% while the fourth laundering cellulose has a water content of 1.98%. Furthermore, the determination of ash content in the cellulose from wood fiber rubber washing results.

The ash content indicates the rich content of metal oxides or mineral salts and impurities contained in the cellulose from wood fiber washing results. Based on the National Indonesian standard criteria for adsorbent ash content is a maximum of 2.5%. Table 2 shows that the ash content of cellulose from wood fiber rubber decreases with decreasing water content. Based on the data in Table 2, it is known that cellulose from wood fiber washery four times has the lowest ash content is 0.92% in accordance with the terms of a maximum ash content of the adsorbent, to cellulose from the washing 1x, 2x, and 3x exceeds the maximum ash content of an adsorbent.

Identification and Characterization of Natural Kaolinite and Activation using FT-IR spectrophotometer

Kaolinite has the characteristics of the bond, Si-O (wavenumber area around of 993, 1024, and 1112 cm^{-1}), Si-O-Al (in the area around of 530 cm^{-1}) and OH (in the wavenumber area around of 3684, 3668, 3651, and 3618 cm^{-1}) (Spence and Kelleher, 2012). Vibration typical kaolinite which show ties to the kaolinite presented in Table 2.

Table 2. Data for kaolinite wave numbers

Wavenumbers (cm^{-1})	Vibrations
3670-3656	Bend (Al-OH)
3435-3433	Bend HOH
1635-1629	HOH Stretch
1100-1005	bend the Si-O
916-915; 888-842	O-H deformation bound cations
542-535	Bending Si-O-Al
475-468	Stretch Si-O-Si

(Saikia *et* al, 2010)

In Figure 3a looks a typical absorption band at natural kaolinite in the area of wave number 3695.6 cm^{-1} and 3618.4 cm^{-1} that indicates Al-OH stretch vibration which is characteristic of kaolinite. Uptake in the area of 3448.7 cm^{-1} and 1635.6 to 2368.5 cm^{-1} may indicate vibration OH observed almost in all silicate hydrate. Bond at 3448.7 cm^{-1} indicates the stretch vibration of HOH and 1635.6 cm^{-1} indicates HOH bending vibration. Strong absorption band appears at wavenumber 1026.1 cm^{-1} and 1002 cm^{-1} which show the stretch vibration of Si-O as tetrahedral layers of kaolinite, while uptake in areas 918.1 cm^{-1} indicates Al-OH bending vibration as octahedral layers of kaolinite. Vibration strain Si-O-Al appears at 547.7 cm^{-1}, while the strong absorption bands appear on the area 470.6 cm^{-1} and 401.1 cm^{-1} that indicates the bending vibration of Si-O-Si (Saikia and Parthasarathy, 2010).

Natural kaolinite which has been characterized using FT-IR spectrophotometer is then performed the activation process. There are two stages in the activation process kaolinite namely heating at 400˚ C for two hours and acidification using sulfuric acid (H_2SO_4) with various concentrations of 1%, 5%, 10% and 15%. Activation by heating at a temperature of 400º C aims to remove impurities such as alkali metal or alkaline earth metal contained in the natural kaolinite (Gao et.al, 2016). Absorption bands seen in Figure 3b

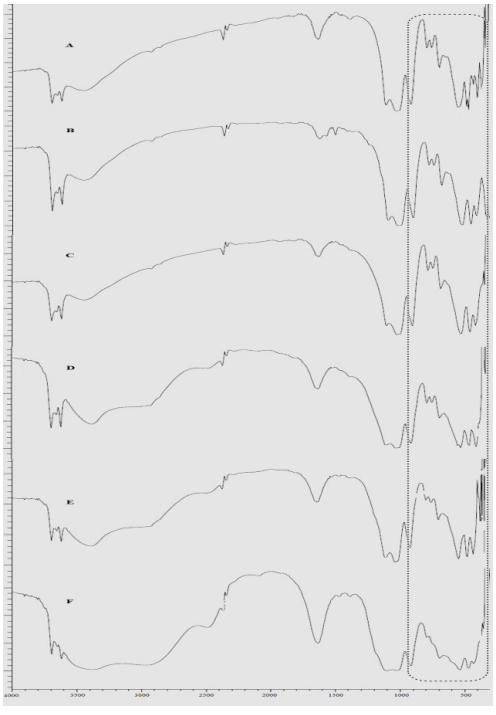

Figure 3. FT-IR spectrum of (A) a natural kaolinite; (B) kaolinite heating; and acidification result kaolinite H_2SO_4 (C) 1%; (D) 5%; (E) 10%; and (F) 15%

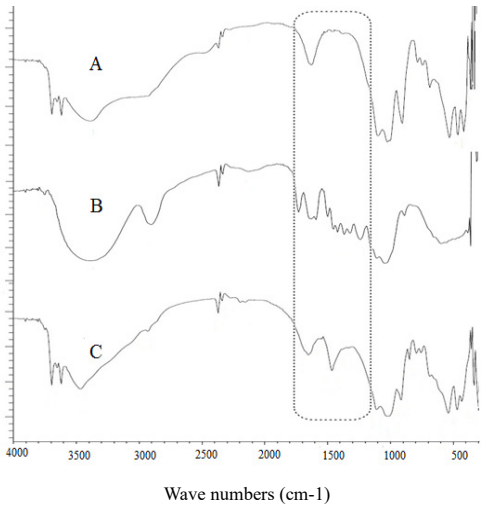

Figure 4. FT-IR spectrum of (a) kaolinite result of acidification of H_2SO_4 10%; (b) the cellulose of the wood fibers result laundering 4x; (c) kaolinite impregnated cellulose from wood fiber rubber

shows the shift in the bending vibration of Si-O appearing at wave number 1018.4 cm^{-1} and stretch vibration of Si-O-Al appearing at 540.07 cm^{-1}. Al-OH stretch vibrational still appears at wave number 3695.6 cm^{-1} and 3618.4 cm^{-1}. Vibration bend and stretch HOH appear on the same wave numbers with natural kaolinite, which is 3448.7 cm^{-1} and 1635.6 cm^{-1}. Vibration bending Si-O-Si remains on the wave number of 470.6 cm^{-1}.

For activation using strong acids will produce kaolinite with active sites larger and larger surface acidity that will produce kaolinite with a higher adsorption capacity than before is activated (Wang et.al, 2016). From Figure 3 presented shows that the FT-IR spectrum of shifting, especially again in Figure 3e which result kaolinite acidification H_2SO_4 10%. Absorption bands seen in Figure 3e shows the shift of the HOH bending vibration that appears at wave number 3387 cm^{-1}, Si-O stretch vibration that appears at wave number 1103.2 cm^{-1} and 1033.8 cm^{-1} and bending vibration Al OH which appears at wave number 910.4 cm^{-1}. Al-OH vibrational strain persists at 3695.6 cm^{-1}. Vibration stretch HOH remains on the wave number 1635.6 cm^{-1}.

Identification and Characterization of Kaolinite Result of impregnation with Wood Fibers Cellulose Rubber using FT-IR spectrophotometer

Impregnation process kaolinite with rubber wood cellulose fiber made from mixing the two solutions. The solution I consisted of a mixture of 1.5 M NaOH and thiourea 1 M and then added cellulose from wood fiber 4x rubber washing results. Solution II consists of kaolinite results of acidification H_2SO_4 10% and 46% NaOH is added and ice cubes. The FTIR spectrum of kaolinite was presented in Figure 4.

From the Figure 4, it seen there are several groups making up the cellulose structure which -CH vibration that appears at wave number 2931.8 cm^{-1} and strengthened also by the emergence of vibration in wave numbers 1465.9 cm^{-1} and 1342.4 cm^{-1}. This suggests that the cellulose compound capable of sticking and bonding with kaolinite. Absorption bands are seen in Figure 4c. From the Figure 4, it can see the shift of the HOH bending vibration that appears at wave number 3464.1 cm^{-1} with a strong intensity. Al-OH vibrational stretch that is characteristic of kaolinite persists at 3695.6 cm^{-1}. Si-O vibrational stretch as tetrahedral layers

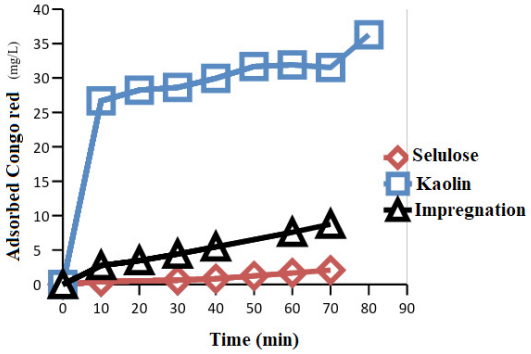

Figure 5. Effect of contact time Congo red 40 mg / L with adsorbent cellulose from wood fiber gum (control), kaolinite activated (control), and kaolinite impregnated cellulose to the amount of Congo red adsorbed

of kaolinite and Al-OH bending vibration as octahedral layers of kaolinite persists at 1026.1 cm^{-1}, 1010.7 cm^{-1} and 918.1 cm^{-1}. Vibration strain Si-O-Al remains on the wave number 540.07 cm^{-1} and bending vibrations of Si-O-Si also persists in the area of 470.6 cm^{-1} and 432.05 cm^{-1}. Vibrations that appear in the FT-IR spectrum of Figure 4c has a lower intensity, due to the merger of two of the compounds causing the concentration contained in each of these compounds is reduced.

Impregnation process involves physical interaction between cellulose impregnated with kaolinite. This physical interaction occurred at the surface and are the result of physical force or involve intermolecular forces such as Van der Waals bonding. The success of the impregnation process can be seen in the FT-IR spectrum of Figure 4 wherein the cellulose constituent is -CH group appears at wave number 2931.8 cm^{-1} and reinforced with vibration at wave number 1465.9 cm^{-1} and 1342.4 cm^{-1} kaolinite and the new FT-IR spectrum is shown in Figure 4c.

Effect of Time Adsorption of Dye Congo Red using Adsorbents Kaolinite Activated (Control), Cellulose Results Laundering (Control), and Kaolinite impregnated cellulose and Determination of Kinetic Parameters

Effect of adsorption time to dye adsorption Congo red is done by encounters 0.03 g each adsorbent with dye solution is Congo red 50 mL with a concentration of 40 mg/L. The adsorption process carried out with stirring during the adsorption contact time varied i.e. for 10 to 120 minutes. The observation of the effect of contact time dye adsorption Congo red with activated kaolinite, cellulose washery and kaolinite impregnated cellulose can be seen in Figure 5.

Figure 5 shows a concomitant increase in the adsorption amount of Congo red is absorbed relatively increased. At adsorbent cellulose from wood fibers visible rubber dye number Congo red increased continuously in time from 10 minutes to 70 minutes, but a decline in the next adsorption time increment. At the time of 70 minutes showed amount of Congo red the greatest adsorbed i.e. 2.08 mg/L. On kaolinite adsorbent activated seen amount Congo red adsorbed increased in 10 minutes to the 80 minutes. At the time of 80 minutes showed amount of Congo red the greatest adsorbed i.e. 36.29 mg/L. Whereas in kaolinite adsorbent impregnated cellulose also showed an increase in the time of 10 minutes until 40 minutes. At 60 minutes the amount of Congo red adsorbed decreased, but increased again to 70 minutes and further declined in the next time increment. At 70 minute, kaolinite impregnated cellu-

Table 3. Parameter kinetic adsorption of Congo red to the adsorbent cellulose from wood fiber, activated kaolinite, and kaolinite impregnated cellulose

Adsorbent	k_1 (min^{-1})
Activated Kaolinite	0.026
Impregnated Kaolinite	0.002
Cellulose	0.001

lose has the number of Congo red largest adsorbed i.e. 8.75 mg/L.

Adsorption time data in Figure 5 can be used to determine the kinetic parameters of adsorption. Adsorption rate constant (k1) Congo red on each adsorbent using Langmuir-Hinshelwood equation. Data adsorption rate constant dye Congo red on each adsorbent is presented in Table 3.

Table 3 shows that the activated kaolinite adsorbent having adsorption rate (min^{-1}) that is larger 0.026 min^{-1}, kaolinite adsorbent impregnated cellulose has the adsorption rate of 0.002 min^{-1} while the adsorbent cellulose from wood fiber rubber have very little adsorption rate which is equal to 0.001 min^{-1}. This is because adsorbate that in this study dye Congo red adsorbed on an adsorbent layer and the surface of the kaolinite activated causing the adsorption rate faster than kaolinite adsorbent impregnated cellulose and cellulose from wood fiber gum. Whereas in kaolinite adsorbent impregnated cellulose from wood fiber and rubber adsorption occurs in physics involving Van der Waals bonds, so that the adsorption rate is slower.

Effect of Temperature and Concentration of Congo red and Determination of Thermodynamic Parameters

The effect of Congo red dye adsorption temperature by cellulose adsorbents from rubber wood fibers, activated kaolinite, and cellulose impregnated kaolinite is presented in Figure 6, 7 and 8. In Figure 6, 7, and 8 it is seen generally that the greater the temperature (°C) and the concentration (mg/L) the amount of Congo red adsorbed (mg/L) is also relatively increased, but some are decreasing at some temperature and concentration. The adsorption thermodynamic parameters include adsorption capacity (b), adsorption energy (E), enthalpy (ΔH), and entropy (ΔS). The adsorption capacity data for each adsorbeWnt is presented in Table 4.

Table 4 shows that the activated kaolinite adsorbent has the largest adsorption capacity of 1000 mg/g at 70 °C, whereas the cellulose impregnated kaolinite adsorbent and the cellulose adsorbent of rubber wood fibers at 40 °C and 50°C have the largest adsorption capacity of 500 mol / g and 125 mol / g. In Table 4 also presents the adsorption energy data (E) which shows on every adsorbent in general an increase in adsorption energy as temperature increases. In the cellulose adsorbent of rubber wood fibers (control) has the greatest energy at 50 °C of 4.96 kJ /mol, the activated kaolinite adsorbent (kaolinite) at 70 °C has the greatest energy of 10.22 kJ/mol, the impregnated kaolinite adsorbent at 40 °C has the greatest energy of 11.09 kJ/mol. The value of adsorption energy can be used to determine the type of adsorption that occurred i.e. physical adsorption or chemical adsorption (Isahak et.al, 2013). Thus the adsorption in this research can be classified as physical adsorption. Other thermodynamic parameters, such as enthalpy (ΔH) and entropy (ΔS) are presented in Table 5.

The entropy value (ΔS) of Congo red adsorption by each of the adsorbents presented in Table 5 indicates a decrease in the degree of irregularity with increased Congo red (mg/L) concentration. This shows the regularity of the Congo red dyestuff absorbed on each adsorbent. In addition to the enthalpy value (ΔH) of Congo red adsorption also decreases with increasing concentration.

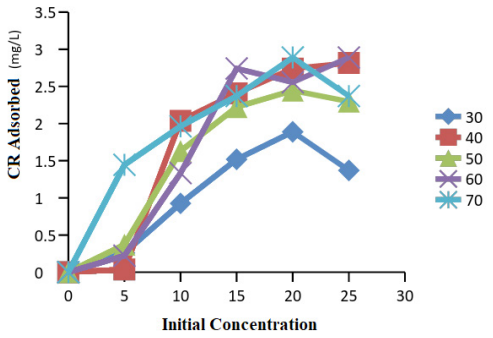

Figure 6. The effect of adsorption temperature and Congo red dye concentration on the amount of Congo red adsorbed by adsorbent of cellulose from rubber wood fiber

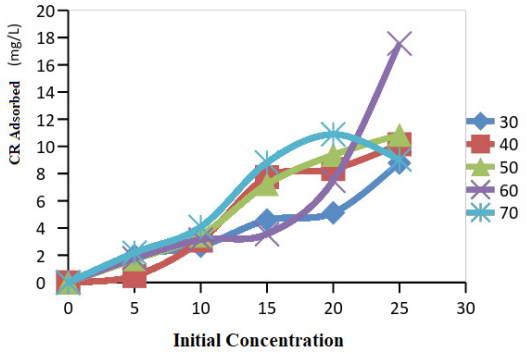

Figure 7. The effect of adsorption temperature and Congo red dye concentration on the amount of Congo red is adsorbed by activated kaolinite

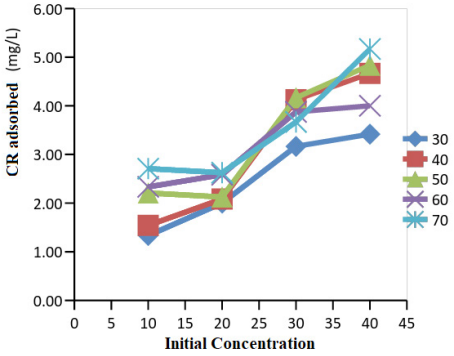

Figure 8. The effect of adsorption temperature and Congo red dye concentration on the amount of Congo red is adsorbed by impregnated cellulose kaolinite

CONCLUSION

The impregnation process involves the physical interaction between kaolinite and impregnated cellulose. This physical interaction occurred involving Van der Waals interaction. From the FT-IR spectrum data the kaolinite impregnation process with successful cellulose is characterized by wavenumbers 432.05 cm^{-1}, 918.12 cm^{-1}, 1026.13 cm^{-1} and the appearance of peaks at wave numbers 2931.8 and 1465.9 cm^{-1} which shows the presence of the -CH group as the structural constituent of cellulose.

The adsorption process is studied through parameters of adsorption time, temperature, and Congo red concentration. The activated kaolinite adsorbent (control) adsorption process was optimum at 80 minutes, 70 °C and 5 mg/L with adsorption energy

Table 4. Thermodynamic parameters (adsorption capacity and energy) of Congo red dye adsorption by cellulose adsorbents from rubber wood fibers (control), activated kaolinite (control) and impregnated kaolinite cellulose.

Adsorbent	T (°C)	R^2	b (mol/g)	E (kJ/mol)
Kaolinite activated (control)	30	0.988	333.33	6.19
	40	0.901	500	4.87
	50	0.949	500	3.72
	60	0.958	200	5.31
	70	0.985	1000	10.22
Kaolinite impregnated cellulose	30	0.914	250	9.47
	40	0.906	500	11.09
	50	0.996	250	7.83
	60	0.997	166.67	5.87
	70	0.866	142.86	5.17
Cellulose	30	0.904	37.04	0.35
	40	0.996	125	4.82
	50	0.935	111.11	4.96
	60	0.943	111.11	2.35
	70	0.940	100	3.32

Table 5. Thermodynamic parameters (enthalpy and entropy) of Congo red dye adsorption by cellulose from rubber wood fibers, activated kaolinite, and impregnated cellulose kaolinite

Adsorbent	C_o	R^2	ΔH (kJ/mol)	ΔS (kJ/mol)
Cellulose (control)	5	0.933	112.45	0.32
	10	0.948	48.88	0.13
	15	0.996	18.92	0.05
	20	0.983	10.09	0.02
	25	1.000	22.70	0.06
Kaolinite activated	5	0.977	61.07	0.18
	10	0.998	12.94	0.038
	15	0.717	7.80	0.030
	20	0.999	15.36	0.050
	25	0.970	14.23	0.046
Kaolinite impregnated cellulose	10	0.956	19.72	0.054
	20	0.866	7.37	0.010
	30	0.793	12.83	0.029
	40	0.728	8.89	0.015

of 10.22 kJ/mol. The impregnated cellulose kaolinite adsorbent undergoes optimum adsorption at 70 minutes, 40 °C and 10 mg/L concentration with adsorption energy of 11.09 kJ/mol. The cellulose adsorbent of rubber wood fibers undergoes optimum adsorption process at 90 min, 50 °C and 5 mg /L with adsorption energy of 4.96 kJ/mol. In this study showed that adsorption occurs in the form of physical adsorption.

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