INTRODUCTION

One of the clay mineral resulting from volcanism is bentonite. The existence of bentonite is very abundant in nature Indonesia, cheap, and easily available (Mar et al., 2013). As an inorganic material, bentonite has different capabilities with other inorganic material, which can swell and has a layered structure (Barast et al., 2017). Bentonite has been used as adsorbent and methods modifications have also been developed, such as intercalation, insertion and pillarization. One of modification of bentonite clay that has not been done is the impregnation methods.

The impregnation is physically solid attachment process with an adsorbent material. Impregnation is used to increase the adsorption capacity and selectivity of an adsorbent (Pandey, 2017). Impregnation generally used as a method for modifying an organic material with other organic material or with inorganic materials. The organic material used as a modified clay material in the form of cellulose. Cellulose has many advantages because it is used in various fields such as apparel and fiber, wood and paper, pharmaeutical and cosmetic industries and also for adsorbent of waste water and heavy metals (Orlandi et al., 2017).

Cellulose, hemicellulose and lignin contained in the wood fiber gum. The presence of cellulose, hemicellulose and lignin made of rubber wood fiber can potentially be used as an absorbent material. Fiber is also environmentally friendly because it can be degraded biologically. The existence of abundant wood fiber, easily available and inexpensive because it comes as a byproduct of the wood processing industry (Suhas et al., 2016).

The development of textile industry, which grew rapidly results in increased of waste water that enter into water system in the form of dye. Congo red dye as an organic substance synthesis is one of the waste products produced by the textile industry. Congo red dye are azo group (RN = NR) is red, toxic and difficult to be degraded as a complex chemical structure and the presence of aromatic rings (Munagapati and Kim, 2017; Bharali and Deka, 2017).

In use as a textile dye in tirth country waste water containing congo red dye not handled well, even dumped directly into the environment. One of the intense use for textile dye is congo red. If congo red substance direct contact to humans it can cause some diseases such as allergies, skin irritation, dermatitis, mutations in the body, it can even cause cancer. Removal of congo red has been investigated by adsorption using various adsorbent such as hydroxides (Said and Palapa, 2017), metal organic framework based materials (Zhao et al., 2017), porous materials (Lei et al., 2017), and also zeolites (Liu et al., 2014).

Impregnation of bentonite was conducted by many researchers for various application. Garade et al. (2010) was used dodeca-tungstophosphoric acid for impregnation of bentonite and material was used as catalyst of hydroxylation of p-cresol. Bentonite also impregnated with titanium oxide for degradation of methylene blue (Rossetto et al., 2010). Functionalization of bentonite also was achieved by impregnation, which was used nanoparticles as impregnant (Amadio et al., 2017).

In this study, impregnation of bentonite with cellulose was conducted. Material was used as an adsorbent for congo red dye in aqueous medium. The interaction parameters tested between congo red and adsorbent in the adsorption process were the influence of time, concentration, temperature and pH. In order to determine the residual concentration (mg/L) and the amount of congo red adsorbed (mg/L) adsorbent activated bentonite (control) and bentonite impregnated cellulose were then analyzed using a UV-Vis spectrophotometer.

**ABSTRACT**

The process of bentonite impregnation with cellulose has been studied. Cellulose extracted from rubber wood and clay from natural bentonite was activated. The impregnation process is performed using thiourea as impregnant agent. The impregnation results were characterized by using FT-IR spectrophotometer then the material was used as congo red dye adsorbent. Factors affecting the adsorption process were studied by kinetic parameters and thermodynamic parameters. The FTIR results indicate the impregnation process was successfully conducted the characterization by FTIR indicated resources of typical absorption of the hydroxyl (OH) and vibrational (-CH) vibration function groups as specific groups of cellulose Appearing at wave numbers 3464.15 cm\(^{-1}\) and 609.51 cm\(^{-1}\) from impregnated material. Vibration Si-O-Si and Al-O-Si as bentonite-specific strands groups Appear at 1465.9 cm\(^{-1}\) and 609.51 cm\(^{-1}\) wavenumbers in the impregnated spectra. The adsorption thermodynamic study showed that the adsorption and adsorption capacity of the cellulose-impregnated bentonite adsorbent reached the optimum point at 50 °C at 43.47 mol/g and energy of 11.62 kJ mol. The optimum enthalpy (ΔH) of cellulose bentonite was 143.13 kJ/mol and the minimum entropy (ΔS) at concentration of 40 mg/L was 0.207 kJ/mol.

Keywords: Bentonite, cellulose, impregnation; adsorption; Congo red

**IMPREGNATION OF BENTONITE WITH CELLULOSE AS ADSORBENT OF CONGO RED**

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EXPERIMENTAL SECTION

Chemicals and Instrumentation

The materials used in this study are wood fiber (± 60 mesh), hydrochloric acid (HCl), bentonite (Al₂O₃·4SiO₂·xH₂O), dye congo red (C₃₆H₂₈N₂Na₂O₁₀S₂), sulfuric acid (H₂SO₄), sodium hydroxide (NaOH), thiourea (H₂NCSNH₂) and distilled water (H₂O). The instruments were thermometer, hotplate, oven, furnace, horizontal shaker, FTIR spectrophotometer (Shimadzu prestige-21) and UV-Vis spectrophotometer (Thermo Scientific Genesys 20).

Methods

Preparation of Cellulose Fibers from Wood Dust

A total of 100 g of wood fibers soaked into hydrochloric acid (HCl) 0.1M for 3 hours stirred and then filtered, the solid is taken and then rinsed with distilled water, followed by immersion using 0.1 M NaOH for 3 hours stirred and then filtered and the solids washed with distilled water until the filtrate water has pH neutral. The process of soaking by HCl and NaOH was four times repetition to get cellulose that agrees or approaching standard cellulose characteristics. The residue was dried and then characterized using FTIR spectrophotometer and detemine of the moisture and ash content. The characterization results were compared to standard cellulose.

Determination of moisture and ash content of cellulose from wood fiber

A total of 1 g of cellulose put in a petri dish that known weight and heated in an oven at 110°C for 5 hours and then weighed until gain constant weight and counted the percent moisture content of cellulose. For detemriment of the ash content of the cellulose was heated at 400°C in a furnace for 3 hours. The ash formed and then determined to the moisture percent of ash content of cellulose.

Bentonite activation

Bentonite preparation procedure was performed according to Ozcan (2004). A total of 100 g natural bentonite is heated using the furnace at a temperature of 400°C for 2 hours and then allowed to stand at room temperature and than followed by acidification process. Acidification is done by dissolving 50 g of bentonite into 250 ml of sulfuric acid (H₂SO₄) 1 M for 2 hours. The suspension is allowed to stand until the precipitate formed and filtered. Furthermore bentonite which has been prepared called bentonite activated. Natural bentonite and natural bentonite heated at a temperature of 400°C and natural bentonite results from acidification using sulfuric acid (H₂SO₄) were characteristic using FTIR spectrophotometer.

Bentonite impregnation with cellulose

Amount of 2 g of cellulose was added to a mixture of 0.6 M NaOH solution and the solution of thiourea 1 M. The mixture was stored at 0°C for 4 hours to obtain a solution (I). A total amount of 10 g of bentonite was mixed with NaOH 46% as much as 16 ML in ice water for 6 hours while stirring with a magnetic stirrer. Ice as much as 26 g was added to obtain a solution (II). The solution (I) and (II) are mixed and stirred with a magnetic stirrer for 30 minutes and then a few drops of the solution of H₂SO₄ 5% evenly to the solid results obtained impregnation and left for 1-2 hours. The solids are washed with distilled water and ready to be used as absorbent characterized using FTIR spectrophotometer.

Preparation of congo red dye stock solution

A total of 1 g congo red dye dissolved in distilled water in a 1 L flask to obtain a concentration of 1000 ppm.

Preparation of standard solution of Congo red

The standard solution of congo red dye prepared by diluting the stock solution into to standard solution with a concentration of 5, 10, 15, 20, 25, 30, 40, and 50 mg/L.

Effect of adsorption time

The amount of 0.03 g absorbent of the activated bentonite (control), wood fibers (control) and bentonite impregnated cellulose was added into the 50 mL congo red solution with a concentration of 40 mg/L. Before the adsorption process the first measurement of pH of the mixture and adjusted to the initial pH. The adsorption process has taken place at 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. The adsorbent then separated from the solution using centrifugation and the congo red dye concentration in the solution after interaction was measured using a UV-Vis spectrophotometer. The amount of residual concentration (mg/L), the amount of congo red dye adsorbed (mg/L) was calculated using the equation of the calibration curve of standard solution, while the rate of adsorption (k) is calculated using the equation of Langmuir-Heinselwood.

Effects of concentration and temperature adsorption

The influence of thermodynamic adsorption congo red dye by activated bentonite (control), cellulose and bentonite extraction results impregnated cellulose is done through a series of experiments with varying concentrations of congo red dye adsorption and temperature. Adsorbent activated bentonite (control) of 0.03 g and 0.03 g of bentonite impregnated cellulose was mixed with 50 mL of congo red dye (40, 30, 20, 10 and 0 mg/L). While the extraction of cellulose (control) is added to 50 mL of congo red dye at a concentration (25, 20, 15, 10, 5 and 0 mg/L). The adsorbent which has been mixed with the congo red dye measured pH using a pH meter and adjusted to the initial pH congo red dye that has previously been known then the mixture 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 congo red dye that has separated from the adsorbent measured absorbance values using a UV-Vis spectrophotometer to determine the concentration of residual congo red dye after the adsorption process. The adsorption capacity (b), the adsorption energy (E) can be calculated using the Langmuir equation, while the adsorption enthalpy (ΔH), and the adsorption entropy (ΔS) can be calculated using thermodynamic equation.

RESULTS AND DISCUSSION

Determination of Moisture and Ash Content of Cellulose

The moistures and ash content of the wood fiber after the acidification treatment using 0.1 M hydrochloric acid and followed by immersion using 0.1 M sodium hydroxide acidification process and immersion with a base made 4 times and each time the treatment was measured moisture content and ash content contained therein. After going through this process is expected to obtain cellulose that is free of impurities and other macromolecular compounds such as lignin and hemicellulose. Unwanted compounds including such impurities will form a salt and water molecules when reacted with hydrochloric acid and sodium hydroxide. The resulting salt has a great solubility in water, so that impurities in the form of...
the salt will be lost during the washing process until a neutral pH. Determination of water content is done at a temperature of 110°C using the oven, while determination of ash carried out at a temperature of 400°C using a furnace. Results of the determination of moisture content and ash content of cellulose are presented in Tables 1.

The moisture content as presented in Table 1 shows the hydrate water which can be removed by heating 110°C. The water content must be determined in a material because it relates to the use of such materials. In general, the desired moisture content has low water content. It also relates to the retention time of the material to be used in this case is cellulose washing results. If the high water content in the storage cellulose cellulose cannot be done in a longer period of time with limited use anyway. In this study, treatment outcome cellulose has relatively low water content in the range of 1.98 to 6.52% (w/w). Acidification and soaking treatment with a base that is repeated causing the water content owned cellulose decline. Furthermore, the determination of ash content in the cellulose washing results as presented in Table 1. The ash content indicates the content of metal oxides contained in the cellulose washer. Metal oxides in cellulose as presented in Table 1 is derived from elements of macro and micro nutrients that exist in plants that in this case derived from wood fibers. The more the process of leaching with acid and base will cause a decrease in ash content. The process of soaking with acid and bases as much as 4x produce low ash content which amounted to 0.91% (w/w). Results of the determination of moisture content and ash content in the cellulose cannot be the basis of success and purity cellulose extracted from wood fiber and therefore need to proceed with spectroscopic characterization using FT-IR spectrophotometer.

### Cellulose Characterization of Wood Fiber Extraction Results Using FTIR Spectrophotometer

Prior to the extraction of cellulose, the first made of wood fiber identification using FT-IR and compared to the FT-IR spectrum of standard cellulose. Comparison of FT-IR spectrum of a standard cellulose and cellulose prior to purification is presented in Figure 1. shows FT-IR spectra of a standard cellulose showed absorption at 3348.2 cm⁻¹ which is the stretching vibration of the hydroxyl group (OH). Wavenumber at 2900.4 cm⁻¹ indicates -CH vibration which is a constituent group of the cellulose structure and reinforced with vibration at wavenumber 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 wave number 1250-1030 cm⁻¹ and a stretching vibration.

The wave number 3410.15 cm⁻¹ indicates the presence of hydroxyl (OH), the wave number 2924.09 cm⁻¹ indicates the group -CH reinforced with vibration at wave number 1427.32 cm⁻¹, 1327.03 cm⁻¹ and in the fingerprint region that is at 1250-1050 cm⁻¹ for ether group (-CO). In the FT-IR spectra showed similarities with the standard cellulose cellulose before extracted. In the FT-IR spectra of cellulose gum wood still visible tops of unwanted vibration is the wave number 1600-1700 cm⁻¹ that indicates aromatic structure of lignocellulose constituent. Therefore necessary advanced separation processes in order to obtain a standard cellulose cellulose approaching.

Cellulose extraction process aim to separate cellulose from compounds undesirable done by soaking the wood fibers using hydrochloric acid at a concentration of 0.1 M for three hours followed by immersion using sodium hydroxide at a concentration of 0.1 M for three hours. The extraction process is done with 4x repetition. Han (Manzato et.al, 2017) states that immersion using HCl is used to break the hemicellulose and lignocellulose while NaOH solution is used to break the hemicellulose and lignocellulose while NaOH solution is used to dissolve the lignin, hemicellulose and other compounds in order to get closer to the characteristics of the cellulose stan-

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**Table 1. Data cellulose moisture and ash content of the wood fiber**

| Washers Cellulose | Water Content (% w/w) | Water Content (% w/w) |
|-------------------|-----------------------|-----------------------|
| 1x                | 6.52                  | 6.86                  |
| 2x                | 4.85                  | 6.73                  |
| 3x                | 3.96                  | 6.00                  |
| 4x                | 1.98                  | 0.91                  |

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Figure 1. FT-IR spectrum of a standard cellulose (A); Cellulose before washing with HCl and NaOH (B); Cellulose 4x washing (C); Cellulose 3x washing (D); Cellulose 2x washing (E); Cellulose 1x washing (F)
Characterization of Natural and Activated Bentonite using FTIR spectrophotometer

Characterization of functional groups in the natural bentonite, natural bentonite heating at 400 °C and natural bentonite acidified with H2SO4 were used FTIR spectrophotometer. FT-IR spectrum characterization results are presented in Figure 2. The natural bentonite (Figure 2a) at wave number 3448.7 cm⁻¹ and 1635.6 cm⁻¹ indicating a vibration of tensile and bending of HOH, explain the water content in the bentonite which acts as interlayer molecules. Peak at wave number 3626.1 cm⁻¹ and 910.4 cm⁻¹ indicates the presence of a stretch of AlO-(OH)-Al and buckling AlO-(OH)-Al indicating the octahedral layers of bentonite. Strong intensity at 1033.8 cm⁻¹ seen the peak of the stretch of Si-O-Si as the tetrahedral layer of bentonite, and vibrational bending Si-O-Si appears at 470.6 cm⁻¹. Peaks appear at 532.3 cm⁻¹ indicate of the vibration of buckling Al-O-Si and an absorption band that appeared at 686.6 cm⁻¹ indicates vibration of the mineral feldspar, which is associated in mineral bentonite.

After characterization of bentonite using FTIR spectrophotometer, the next process is the preparation phase is done by heating at a temperature of 400°C and acidification using sulfuric acid (H2SO4) Natural bentonite heating temperature of 400°C is shown in Figure 2b. Peaks that appear in the FT-IR spectra of heating results did not show much different compared to the vibration generated in the FT-IR spectra of natural bentonite. Peak shifting shown in wave number 3695.6 cm⁻¹ as the vibration of the stretch (Al-OH-Al) and the wave number 694.3 cm⁻¹ that indicates the presence of the mineral feldspar. Other absorption bands appear on the same wave numbers with natural bentonite before preparation.

The heating process at a temperature of 400°C did not show much shift in wave numbers as an indication of the success of the process, so do the chemical preparation by acidification using sulfuric acid (H2SO4) The purpose of acidification with sulfuric acid is to bind to the metals that are small and activates natural bentonite. Figure 2c shows the FT-IR spectra of natural bentonite after acidification process. Absorption band of the stretch (HOH) and bending (HOH) that appears at wave number 3428.5 cm⁻¹ and 1635.6 indicates a shift. Vibratıon of the stretch (Al-OH-Al) shifts the wave number 3672.4 cm⁻¹ and buckling (Al-OH-Al) remained at 910.4 cm⁻¹. In the wave number of 470 cm⁻¹ and 532.3 cm⁻¹ are the vibration from buckling (Si-O-Si) and bending (Al-O-Si) while the mineral feldspar associated with bentonite absorption at wave number 700 cm⁻¹. Declining all transmittance on FT-IR spectra of natural bentonite acidification results followed the changes in the functional groups experienced a shift wave number indicates the success of the preparation process performed on bentonite.

Characterization of Cellulose and Impregnated Bentonite using FT-IR Spectrophotometer

Perior the impregnation process, cellulose and bentonite were characterized using FT-IR spectrophotometer. are presented in Figure 3. The specific groups in cellulose extraction results that OH, -CH₂-O which appears in the spectrum of FT-IR measurement results. -OH group appears at wave number 3387 cm⁻¹ which is OH stretching vibration. The wave number 2908.55 cm⁻¹ indicates
vibration of $-\text{CH}_2$ that the structure of cellulose reinforced by vibration at wave number 2368.59 cm$^{-1}$ and 2137.13 cm$^{-1}$. Stringing group $-\text{CH}_2\text{O}^{-}$ in which cellulose is a polymer of glucose and fructose appear at wave number 1300-1400 cm$^{-1}$.

The process of acidification on bentonite aims to remove small cations and simultaneously activates natural bentonite. This is shown in the FT-IR spectrum that presented in Figure 3. Bentonite which has been acidification with sulfuric acid ($\text{H}_2\text{SO}_4$) shows the typical absorption bands at 3672.4 cm$^{-1}$ which is indicates a stretch vibration Al-O-(OH)-Al, HOH stretch vibration shown in wave number 3425.5 cm$^{-1}$ and vibrational strain Si-O-Si at 1041.5 cm$^{-1}$. Vibrations buckling Al-O-(OH)-Al appear at 910.4 cm$^{-1}$, HOH bending vibration at 1635.6 cm$^{-1}$, vibrational bending Si-O-Si appears at wave number 470.6 cm$^{-1}$ and vibration buckling Al-O-Si appears at 532.3 cm$^{-1}$.

Cellulose and activated natural bentonite were modified by impregnation method. The bentonite impregnated with cellulose was made by addition of a mixture of 0.6 M sodium hydroxide solution and 1 M thiourea solution to the cellulose and the addition of sodium hydroxide 46% on activated bentonite, each solution was mixed with a magnetic stirrer for 30 minutes to produce a cellulose impregnation with bentonite. A mixture of 0.6 M sodium hydroxide solution and a solution of 1 M thiourea aims to form a bond between the bentonite with cellulose. The residue was dried and characterized by FT-IR spectrophotometer. FT-IR spectra of cellulose impregnated with bentonite are shown in Figure 3 with the important vibrations is summarized in Table 2.

### Table 2. Comparison of FT-IR spectra of bentonite, cellulose and impregnated bentonite

| Wave numbers (cm$^{-1}$) | Functional group | Bentonite | Cellulose | Impregnation |
|--------------------------|------------------|-----------|-----------|--------------|
| 3425.58                  | -                | 3387      | 3464.15   |              |
| 2908.65                  | $-\text{CH}$     | 2931.8    |           |              |
| 2368.59                  |                  |           |           |              |
| 1735.93                  |                  |           | 1658.78   |              |
| 1658.78                  |                  |           | 1465.9    |              |
| 1041.56                  | $-\text{Si-O-Si}$| 609.51    | 532.35    |              |
| 532.35                   |                  |           | 470.63    |              |

Effect of Adsorption Time of Congo Red Dye Adsorption by

Activated Bentonite, Cellulose and Impregnated Bentonite

The adsorption contact time was an important factor in the adsorption process. According to the collision theory, the reaction rate depends on the number of collisions per unit time. The more collisions that occur, the faster the reaction takes place until the reaction reach an equilibrium condition.

In this study, the adsorption process of congo red dye by adsorbent bentonite (control), cellulose (controls) and impregnated bentonite performed at a concentration of 40 mg/L congo red with contact time for 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 minutes. Number of congo red dye adsorbed can be seen in Figure 4.

Figure 4 it is shows that the activated bentonite adsorption curve (control) shows an increase in the amount of congo red dye adsorption as the adsorption contact time increases. In the activated bentonite (control) the amount of congo red absorbed in the first 10 minutes was 35.04 mg/L and continued to increase until reaching the optimum time at 120 minutes ie 39.12 mg/L. The congo red dye adsorption process by cellulose indicates that each contact time gives a different effect. At 10 minute contact time absorption is not maximized. This is allegedly because the cellulose active group has not reached its saturation point. The amount of congo red dye absorbed continues to increase until 70 minutes.

From the data it can be seen that the optimum contact time required cellulose to absorb congo red dye is 70 minutes with the amount of congo red adsorbed of 2.08 mg/L.

The congo red dye adsorption curve by the impregnated bentonite showed in the first 10 minutes the amount of congo red absorbed ie 0.17 mg/L and continued to increase until the 80 minute of contact time 7.08 mg/L and reached the optimum adsorption amount at 100 minutes of contact time ie 8.88 mg/L then decreased at 120 minutes to 3.13 mg/L. After reaching the optimum adsorption with increasing contact time, the adsorbent absorbency will decrease. This is because the active groups on the adsorbent have reached the saturation point of absorption so that the adsorbent no longer able to adsorb the adsorbant. From the data in Figure 4 its can be calculated the adsorption rate of congo red dye adsorption on bentonite, cellulose and impregnated bentonite using the Langmuir-Hinshelwood equation

$$\ln\left(\frac{C_0}{C}\right) = k_1 \frac{t}{C} + K$$

where $C_0$ = initial concentration of congo red dye (mg/L)
The data of congo red dye adsorption rate constant on impregnated bentonite is presented in Table 3. Table 3 shows the difference of adsorption rate between bentonite, cellulose and impregnated bentonite. The adsorption rate (minute⁻¹) of the impregnated bentonite result is greater than the cellulose adsorption rate. This may occur because the impregnated bentonite is more reactive than the cellulose and the impregnation has more active groups than the cellulose, whereas the activated (control) bentonite has the largest adsorption rate (minutes⁻¹). This can happen because in bentonite there is a chemical adsorption process where the congo red dye is bonded to it surface by forming chemical bonds and homogeneous systems so that the adsorption rate occurs faster. In the adsorbent of congo red dye on cellulose the process that happened in the form of physical adsorption whose strength is weaker than adsorption by adsorbent bentonit. This is because the adsorption process involves a functional group, so the interaction occurs first between the functional groups and causes the adsorption rate to the congo red dye tends to be slower.

### Table 3. Data of congo red dye adsorption rate constant on impregnated bentonite.

| Adsorbent          | Adsorption rate (minutes⁻¹) |
|--------------------|-----------------------------|
| Bentonite (control)| 0.031                       |
| Impregnated        | 0.002                       |
| Cellulose          | 0.001                       |

### Effects of Temperature and Initial Concentration of Congo Red Dye and the Determination of Thermodynamic Parameters

Determination of the effect of temperature and initial concentration between congo red dye as adsorbant with adsorbent bentonit (control), cellulose (control) and impregnated bentonite were done by interaction of congo red dye with each adsorbents. The adsorption process was carried out at various temperatures 30, 40, 50, 60, and 70 °C for each adsorbent.

The variation of congo red dye initial concentration adsorption by activated bentonite (control), cellulose extracted (control) and impregnated bentonite were performed on congo red dye concentration variations 10, 20, 30, 40 mg/L. The adsorption process were carried out for 30 minutes using a magnetic stirrer. The results of congo red dye interactions with bentonite, cellulose and cellulose impregnated bentonite in

![Figure 4. Curve adsorption of congo red dye by activated bentonite (control), cellulose and impregnated bentonite as adsorbents](image)

![Figure 5. Effect of congo red concentration and temperatures on adsorption of congo red dye on the activated bentonite](image)

| Adsorbent          | T(°C) | R²  | b (mol/g) | E/J/mol |
|--------------------|-------|-----|-----------|---------|
| Activated          | 30    | 0.967 | 1000 | 6.847   |
| Bentonite (control)| 40    | 0.945 | 1000 | 5.667   |
|                    | 50    | 0.624 | 1000 | 7.65    |
|                    | 60    | 0.979 | 500  | 3.042   |
|                    | 70    | 0.854 | 500  | 6.424   |
| Cellulose          | 30    | 0.996 | 125  | 4.82    |
| (Control)          | 40    | 0.935 | 111.11| 4.96    |
|                    | 50    | 0.943 | 111.11| 4.35    |
|                    | 60    | 0.940 | 100  | 3.32    |
|                    | 70    | 0.598 | 6.02 | 2.42    |
| Impregnated        | 30    | 0.294 | 15.38| 8.56    |
| Bentonite          | 40    | 0.965 | 43.47| 11.62   |
| (Control)          | 50    | 0.598 | 6.02 | 2.42    |
|                    | 60    | 0.854 | 500  | 6.424   |
|                    | 70    | 0.951 | 18.86| 0.95    |

| Adsorbent          | C_o  | R²  | ΔH (kJ/mol) | ΔS (kJ/mol) |
|--------------------|------|-----|-------------|-------------|
| Activated          | 5    | 0.816 | 77.51 | 0.258      |
| Bentonite (control)| 10   | 0.974 | 7.751 | 0.032      |
|                    | 15   | 0.997 | 2.639 | 0.014      |
|                    | 20   | 0.919 | 51.55 | 0.171      |
|                    | 25   | 0.903 | 56.56 | 0.186      |
|                    | 5    | 0.933 | 112.44| 0.321      |
| Cellulose          | 5    | 0.933 | 112.44| 0.321      |
| (control)          | 10   | 0.945 | 48.88 | 0.134      |
|                    | 15   | 0.996 | 18.922| 0.048      |
|                    | 20   | 0.983 | 10.09 | 0.018      |
|                    | 25   | 1.000 | 22.697| 0.055      |
| Cellulose          | 10   | 0.912 | 143.13| 0.424      |
| impregnated        | 20   | 0.938 | 107.26| 0.309      |
| Bentonite          | 30   | 0.909 | 34.037| 0.99       |
| (Control)          | 40   | 0.950 | 75.03 | 0.207      |
various temperature and initial concentration can be seen in Figure 5.

The adsorption process at various temperature and initial concentration of the congo red dye shows in Figure 5 the change in the amount of congo red dyes that can be absorbed by the activated bentonite adsorbent (control). The curve shows that the greater the temperature and the congo red concentration, the greater the amount of the congo red dye adsorbed by bentonite (activated). The amount of optimum congo red dye adsorbed by bentonite was seen at 70 °C and 25 mg/L concentration with the amount of 23.07 mg/L. Seen at some points, there is a point that coincide at the concentration of congo red 5 mg/L and 10 mg/L. This is because the amount of congo red absorbed at these concentrations does not show too large a difference.

In the cellulose adsorbent of wood fibers (controls) presented in Figure 6 shows that as the temperature and concentration added increased the amount of congo red adsorbed is less significant. The improvement occurs at temperature 40 °C, its seen that the higher initial concentration and increased temperature the more the amount of congo red dye adsorbed. This causes the cellulose as an adsorbent to be applied at that temperature. While at high temperatures cellulose cannot absorb well is possible because the functional groups on cellulose damaged by the heating process.

In contrast to the adsorbent of activated bentonite (control) and cellulose (control), cellulose impregnated bentonite in Figure. 7 shows the amount of adsorbate congo red dye were adsorbed at high temperature, seen at temperatures of 50, 60 and 70 °C there is a point coinciding with concentrations of 30 mg/L.

Figure 7 shows that there is not much difference in the amount of congo red absorbed in various initial concentration. While at concentrations of 40 mg/L with various temperatures, there was a decrease in the amount of congo red dyes absorbed. This is because the large particle size of the congo red dye cannot be absorbed by the cellulose-impregnated bentonite adsorbent.

Thermodynamic parameters were determined by looking for the values of adsorption capacity (b), adsorption energy (E), enthalpy (ΔH) and entropy (ΔS) of the adsorption process. The amount of adsorbed red congo (mg/L) at the various temperature (°C) can be calculated for some predetermined concentrations. The calculation data of adsorption capacity (b) and adsorption energy (E) were using equation 2.

\[
\frac{C}{m} = \frac{1}{bK} + \frac{1}{b}
\]

Were the value of adsorption capacity (b) can be calculated using the equation as the slope and intercept values of the congo red residual concentration (C) as the x-axis to CR eq / n as the y-axis.

The adsorption capacity data (b) is presented in Table 4.

Table 4 shows that the value of adsorption capacity (b) for each adsorbent is different. In the activated bentonite adsorbent, the largest adsorption capacity is seen at temperatures of 30 °C, 40 °C and 50 °C, at optimum cellulose (control) adsorbent capacity at temperatures of 50 °C and 60 °C. Whereas in impregnated bentonite adsorbs, the largest capacity was seen at 50 °C at 43.47 mol/g.

After obtaining the value of adsorption capacity (b), then the value of adsorption energy (E) in each adsorbent is determined by using the constant value obtained from the equation 2. The adsorption energy (E) was calculated using equation 3.

\[
E = -RT \ln K
\]

Were;
K = equilibrium constant
E = energy adsorption (kJ/mol)
R = constant
T = temperature (K)

The adsorption energy presented in Table 5 shows the largest adsorption energy occurred at 50 °C ie 77.51 kJ/mol for bentonite and 4.96 kJ/mol for cellulose adsorbent (control). The modified adsorbent has the largest adsorption energy compared with the bentonite and the cellulose as control adsorbent. The cellulose impregnated bentonite has optimum adsorption energy at 50 °C i.e. 11.62 kJ/mol.

The other congo red thermodynamic adsorption parameters, such as enthalpy (ΔH) and entropy (ΔS) can be calculated as slope and intercept values of 1/T as the x-axis to ln Kd as the y-axis as shown in equation 4 and the amounts of enthalpy value (ΔH), Entropy (ΔS) are presented in Table 5.

\[
\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

Were;
Kd = distribution coefficient of adsorbate (qe)
ΔH = enthalpy
ΔS = entropy
R = constant
T = temperatures

The activated bentonite adsorbent (control) has the largest enthalpy value at a concentration of 5 mg/L ie. 77.51 kJ. At a temp-
perature of 10 mg/L and 15 mg/L decreased and then again increased at a temperature of 20 mg/L and 25 mg/L. The enthalpy value on the optimum cellulose (control) adsorbent at concentration 5 mg/L was 112.44 kJ/mol then again decreased. Cellulose impregnated bentonite adsorbent has the greatest enthalpy value compared with bentonite (control) and cellulose (control) of 143.13 kJ/mol at initial concentration i.e. 10 mg/L.

Activated bentonit adsorbent (control) has the largest entropy at concentration 5 mg/L that is equal to 0.26 kJ/mol as well as cellulose adsorbent (control) biggest entropy value happened at concentration 5 mg/L that is equal to 0.321 kJ/mol. In bentonit adsorbent impregnated cellulose the largest entropy value at congo red 30 mg/L concentration of 0.99 kJ/mol.

**CONCLUSION**

The FT-IR spectral shows that impregnated bentonite was successful, as seen from the specific functional groups of bentonite and cellulose that appear on the impregnation result. The functional groups that are hydroxyl (OH) and vibrational (-CH) vibrations as specific groups of cellulose appear in wave numbers 3464.15 cm⁻¹ and 2368.59 cm⁻¹ in the impregnated spectra. Si-O-Si and Al-O-Si strands as bentonite-specific groups appear at 1465.9 cm⁻¹ and 609.51 cm⁻¹ wave numbers in the impregnated spectra. The cellulose impregnated bentonite adsorbent reached the optimum adsorption process at minute 120, the extracted cellulose (control) reached optimum condition at minute 90 while the cellulose impregnated bentonite adsorbent reached optimum adsorption process at minute 100 i.e. 8.88 mg/L. The adsorption enthalpy of adsorption of cellulose-impregnated bentonite has the greatest amount compared with bentonite (control) reached optimum condition at minute 90 i.e. 143.13 kJ/mol for reaction enthalpy.

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