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Kinetic and Thermodynamic Adsorption Studies of Congo Red On Bentonite

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Abstract. Adsorption of congo red on bentonite was studied kinetics and thermodynamically. Bentonite was physically activated at various temperatures and characterized using X-ray, and infrared. By increasing thermal temperature activation up to 500 °C can decrease the montmorillonite fraction with decreasing the peak was observed. The kinetic of adsorption suggests that the interaction of congo red-bentonite could be best represented by the first-order kinetics of Langmuir-Hinshelwood model. The adsorption process was exothermic with ΔH in the range -4.43 to -9.76 kJ.mol^{-1} accompanied by increase in Gibbs energy. All results have shown that bentonite after physical activation could be used as an adsorbent for congo red adsorption.

INTRODUCTION

Textile production both in industry and domestic scale will produce dye waste as a by-product of staining process. Usually, the dyes used in the textile production are synthetic dye that composed from complex organic molecule with high toxicity to the environment [1]. One of dye molecule that commonly used in the staining process is Congo red dye as illustrated in fig. 1 [2]. The awareness lack of the people that involved in textile production will conduct pollution to the water bodies in settlement area. It's happened because the dye effluent directly discarded to the water body without any further treatment.

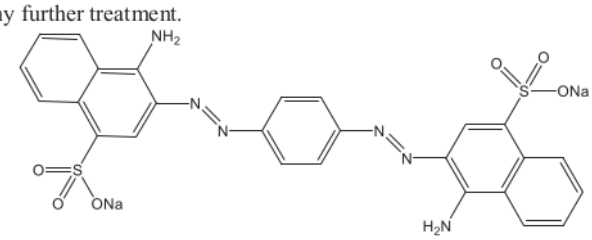

FIGURE 1. Chemical structure of congo red dye

The increasing of dye discharge leads to the many environmental problems. Generally, the molecules are synthetic complex aromatic with high stability and non-biodegradable in natural conditions [3]. Dye contamination to the water body can directly affect the aquatic ecosystem and even human being because of its high toxicity, mutagenic, and carcinogenic properties. In addition, even in small quantities, the dye contamination can be coloring the water body in large scale. That phenomenon can affect the light penetration to the water body and disrupt the photosynthesis proses [4]. Because of its high environmental hazard, the removal of dye contaminant in the environment, especially in a water body, become seriously important.

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The various method including chemical, physical, and biological treatment have been developed to remove the dye contaminant in wastewater disposal [5]. Some of the most studied method for dye removal including coagulation/flocculation, membrane separation, oxidation or ozonation, bioremediation, electro-coagulation, and adsorption [6-7]. Among these methods, adsorption is the most potential method for dye removal because of its economic value and easy to use [6].

Natural clays such as bentonite, kaolinite, and montmorillonite are one of the most potential material to act as an alternative adsorbent [8]. Bentonite abundance in many districts in Indonesia and high surface area and stability properties make bentonite suitably used as a material adsorbent for removal of dye contaminant in wastewater. In spite of this, natural bentonite need special treatment, such as activation and modification, to make it more powerful to use as an adsorbent.

Commonly, there are three most used methods for clay activation, thermal activation, acid activation, and combination between thermal and acid activation. Among these three methods thermal activation is the most technically and economically feasible method for clay activation [9].

In this present work, the congo red removal will be studied by using natural and modified bentonite as low cost adsorbent. Natural bentonite modification is conducted by thermal activation at various temperature. Some of the experimental condition that affecting the adsorption process, including temperature, initial dye concentration, and contact time have been investigated. The rate constant of the adsorption process was calculated by studying the kinetic parameter and the temperature independency of the adsorption process was studied based on the thermodynamic parameter.

MATERIAL AND METHOD

Chemicals and instrumentations

Bentonite clay as adsorbent material in this research was grounded naturally from Sarolangun district, Jambi Province, Indonesia. Congo red dye used in this study was purchased from Sigma Aldrich chemicals and used without further purification. Chemical characterization of thermal activated bentonite clay was performed using FT-IR Shimadzu Prestige-21 using KBr disc in the wavenumber 300-4000 cm^{-1} and Shimadzu X-ray Diffractometer Lab-X type 6000. The sample was scanning at scan speed 1 $deg.min^{-1}$. The dye concentration during adsorption process was monitored using Thermo Scientific spectrophotometer UV-Visible Genesys™ 20 at wavelength 500 nm.

Activated bentonite preparation

Activated bentonite used in this study was thermally activated. The grounded natural bentonite shattered and then washed three times. The clean bentonite then sieved using 150 mesh particle size sieve. Natural bentonite than activated using muffle furnace at any temperatures (200, 300, 400 and 500 ^{o}C). The activated bentonite then stored at isolated flask. Chemical characterization of bentonite before and after thermal activation was performed using FT-IR and XRD analysis.

Adsorption experiments

Adsorption of congo red dye by natural and thermal activated bentonite was conducted in the batch system in 250 mL Erlenmeyer flask. A certain dosage of bentonite adsorbent was dispersed in 50 mL of congo red solution then agitated using an orbital shaker with shaking speed 150 rpm for a certain time to reach the adsorption equilibrium. After the adsorption process, the dye concentration remained in the solution then measured using spectrophotometer UV-Vis.

The amount of dye adsorbed to the adsorbent at any time *t* can be calculated using following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where C_0 is the initial concentration of congo red (mg/L), C_t is the concentration of congo red at any time (mg/L), m is the mass of bentonite adsorbent (g) and V is the volume of congo red used (L).

Kinetic study

The kinetic study of congo red adsorption onto activated bentonite was studied as follows. 50 ml of congo red dye (10, 15, 20, 25 mg/L) was prepared to the 250 mL Erlenmeyer flask. 1 g of thermal activated bentonite then added into the Erlenmeyer and then shake using horizontal shaker with constant speed during specified time (10, 20, 30, 45, 60 and 90 minutes). The solution then filtered and the final dye concentration measured using UV-Vis spectrophotometer. The kinetic data was calculated based on Langmuir isotherm model below:

$$\frac{\ln(C_0/C)}{c} = k_1 \frac{t}{c} + K \tag{2}$$

Where C_0 is initial concentration of procion red dye in the solution, C is the dye concentration after t minutes, t is adsorption time, and K is adsorption equilibrium constant.

Thermodynamic study

The thermodynamic parameter such as enthalpy (ΔH^0), entropy (ΔS^0), and free Gibbs energy (ΔG^0) were determined by varying the adsorption temperature (30, 50, 70 ^{o}C) with constant initial dye concentration. Data obtained than measured using the following equations:

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \tag{3}$$

$$LnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{4}$$

$$K_c = {}^{C_A}/_{C_s} \tag{5}$$

Where C_A, C_s, and K_c are the amount of dye adsorbed on the adsorbent at equilibrium (mg g^{-1}), the dye concentration at equilibrium (mg L^{-1}). R and T are the gas constant (8,314 J mol^{-1} K^{-1}) and adsorption temperature (K).

RESULT AND DISCUSSION

Adsorbent characterization

The XRD powder pattern of the natural bentonite (NB), thermal activated bentonite at 300 ^{o}C (300), thermal activated bentonite at 400 ^{o}C (400), and thermal activated bentonite at 500 ^{o}C (500) were illustrated in Fig. 2. The typical diffraction peak of the natural bentonite that indicate the montmorillonite content was observed at 2θ about 6^o. This peak was observed at all the natural and thermal activated bentonite. Based on Gong et al, [10] bentonite clay, commonly composed by smectite minerals of montmorillonite. However, bentonite is also containing a variety of associated minerals, such as illite, mica, feldspar, calcite, and quartz. Fig. 2, illustrated the diffraction of the associated mineral of the bentonite including, montmorillonite at 2θ of about 20^o and 26^o, illite at 2θ of about 19^o, and quartz at 2θ of about 39^o.

The thermal activation of natural bentonite was conducted at various temperature condition, 300 ^{o}C, 400 ^{o}C, and 500 ^{o}C. After thermal activation, the peak intensity of the montmorillonite was systematically reduced by increasing the activation temperature. This phenomenon indicates the removing of the water molecule that containing in the double layer sheet.

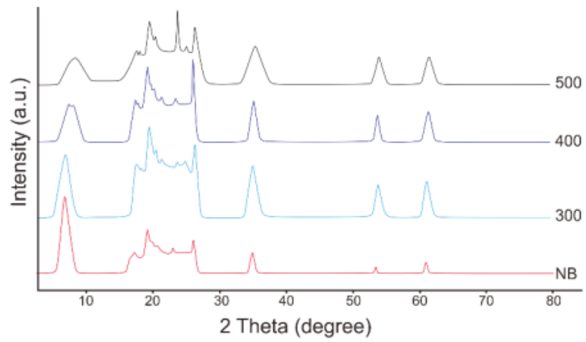

FIGURE 2. XRD pattern of natural bentonite (NB) and thermal activated bentonite at various temperature (300, 400, 500 °C)

The natural bentonite and thermal activated bentonite at 500 °C was characterized using FTIR spectroscopy and the result was illustrated in Fig. 3. The main band characteristic of the bentonite was observed at 3626 cm^{-1} and 910 cm^{-1} as Al-OH-Al stretching and Al-O-Al bending, respectively. The water contain as the interlayer molecule of the bentonite was observed at 3448 cm^{-1} and 1635 cm^{-1} that represent the H-O-H stretching and H-O-H bending respectively. The strong band at 1033 represent the existing of the Si-O-Si stretching vibration [11]. The quartz band, as the associated mineral of bentonite, was observed as weak band at 470 cm^{-1} and 686 cm^{-1} [12].

The FTIR spectra of the natural bentonite and the thermal activated bentonite at 500 °C was not much different. Fig. 3 showed that after thermal activation, the band of H-O-H stretching and H-O-H bending was reduced. This phenomenon indicates that the water content in interlayer of the thermal activated bentonite was reduced.

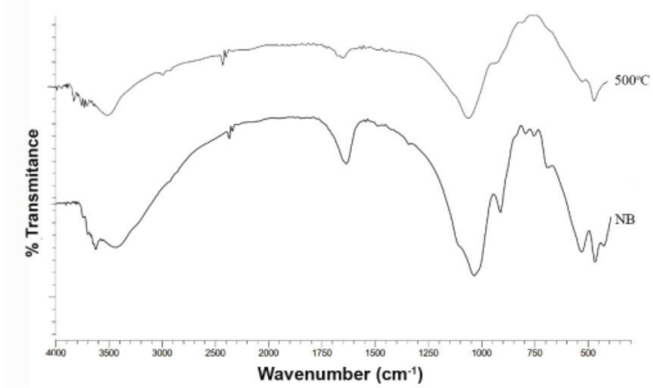

FIGURE 3. FTIR spectra of natural bentonite (NB) and thermal activated bentonite at 500 °C

Effect of contact time and initial dye concentration

In order to study the effect of contact time and initial dye concentration, experiments were conducted with varying the initial dye concentration ranging from 15 to 25 mg L^{-1} and contact time ranging from 10 to 90 minutes. The others factor including stirring speed, dye volume, and amount of adsorbent were kept constant.

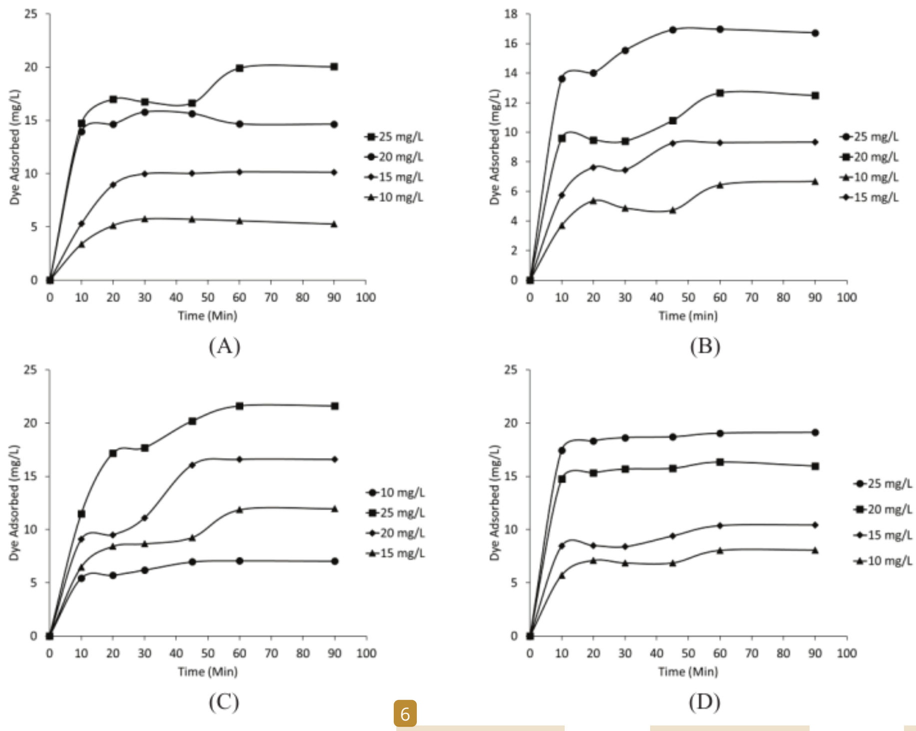

FIGURE 4. Adsorption kinetics of congo red dye onto natural bentonite (A), thermal activated bentonite at 300 °C (B), thermal activated bentonite at 400 °C (C), and thermal activated bentonite at 500 °C, at various initial concentrations.

The effect of adsorption time and initial dye concentration shown in Fig. 4. Based on the adsorption time increased, the amount dye adsorbed increased rapidly within 20 minutes and then get slowly until reached the equilibrium. Moreover, it can be observed that the amount of dye adsorbed onto bentonite adsorbent increased with increasing the initial dye concentration. Commonly, dye removal in adsorption process was depend on the initial dye concentration. Increasing congo red concentration will increase the congo red diffusion in around the bentonite surface due to the increase in driving force of the concentration gradient [13].

Effect of Temperature

The effect of temperature to the amount of dye adsorbed was illustrated in figure 5. The experiment was conducted at various temperature, 30, 50, and 70 °C. based on the Fig. 5, can be observed that by increasing the temperature from 30 to 70 °C, the congo red adsorption was slightly decreased. That phenomenon described that the adsorption process was appeared more favorable occurred in low temperature condition. Moreover, the result described that the adsorption process was exothermic [14].

The effect of temperature to the amount of congo red adsorbed onto bentonite was studied at 30, 50, and 70 °C. The results are described in Fig. 5. From the result can be seen that temperature increase from 30 to 70 °C caused the slightly decreasing of the amount of congo red adsorption in all adsorbent used. This phenomenon indicated that the congo red adsorption onto all adsorbent is slightly exothermic process. Moreover, this observation reveals that the adsorption activity of the congo red onto all bentonite adsorbent is less sensitive to the change of temperature used.

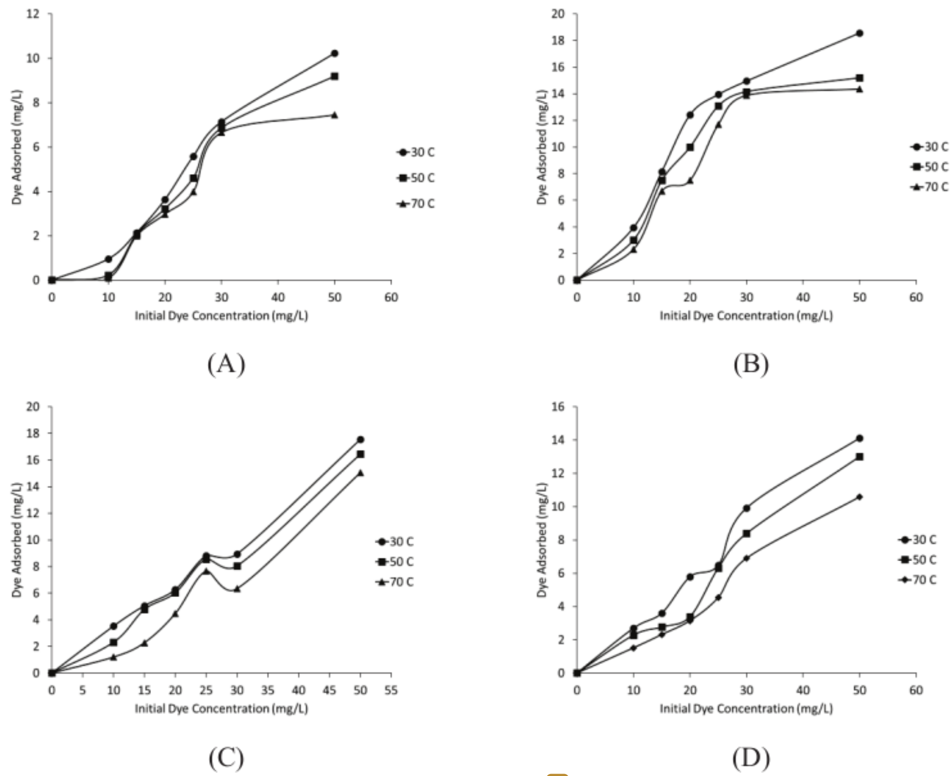

FIGURE 5. Effect of temperature to the adsorption of congo red onto natural bentonite (A), thermal activated bentonite 300 °C (B), thermal activated bentonite at 400 °C (C), and thermal activated bentonite at 500 °C (D)

Adsorption kinetics

The adsorption mechanism pathway can be described based on the chemical kinetic adsorption. The adsorption dependence on the physical and chemical characteristic can be described also based on the adsorption kinetics data. In this study, the kinetics adsorption data was described based on the Langmuir isotherm model. To evaluate the adsorption rate of the congo red onto the natural and thermal activated bentonite, the calculation was based on the assumption that the adsorption process was obeyed the first order of Langmuir isotherm model. The adsorption rate constant (k_1) was measured as the slope from the plot of $\ln(\frac{C_o/C}{C})$ against t/C of from equation 2.

The slope values as the adsorption rate constant (k_1), and correlation coefficient (R^2) from the plot of $\ln(\frac{C_o/C}{C})$ vs t/C was listed in the Table 1. The correlation coefficients obtained are close to unity that indicated the plot provide a straight line. It implies that the kinetic adsorption of congo red onto natural and thermal activated bentonite are well described by Langmuir-Hinshelwood kinetic model [15].

Based on the Table 1, can be seen that the adsorption rate constant (k_1) was dramatically decrease with increasing the initial dye concentration. This phenomenon can be explained based on the surface phenomenon [16]. By increasing the amount of dye molecule in the around of the adsorbent surface, the saturated condition will be quickly achieved. This phenomenon will decrease the reactivity of the adsorbent surface to trap or bond the dye molecule.

TABLE 1. Kinetic parameter based on Langmuir equation for adsorption of congo red onto bentonite

Adsorbent	Initial Dye Concentration	Parameter	
		k_1	R^2
Natural Bentonite	10 mg/L	0.0156	0.971
	15 mg/L	0.014	0.9292
	20 mg/L	0.0136	0.9668
	25 mg/L	0.0133	0.9613
Activated Bentonite (300°C)	10 mg/L	0.0131	0.9167
	15 mg/L	0.0115	0.9503
	20 mg/L	0.0067	0.9643
	25 mg/L	0.0061	0.8993
Activated Bentonite (400°C)	10 mg/L	0.0206	0.9979
	15 mg/L	0.0197	0.9947
	20 mg/L	0.019	0.9593
	25 mg/L	0.0185	0.9289
Activated Bentonite (500°C)	10 mg/L	0.0188	0.9731
	15 mg/L	0.0117	0.9242
	20 mg/L	0.0119	0.9442
	25 mg/L	0.0036	0.9475

Thermodynamic Studies

To evaluate the thermodynamics adsorption parameter in the adsorption system, the amount of dye adsorbed at different temperature was measured. Thermodynamic parameter including Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS), were calculated. The values of the enthalpy change (ΔH) and entropy change (ΔS) were measured as the slop and intercept value of *ln Kc* versus 1/T plot from equation 4. The value of Gibbs free energy change then calculated from the (ΔH) and (ΔS) value obtained based on the equation 3.

The thermodynamic aspect of congo red adsorption onto natural and thermal activated bentonite was presented in Table 2. The value of Gibbs free energy of the congo red adsorption was increase with increasing the adsorption temperature in all adsorbent condition. This phenomenon gave more confirmation about the exothermic adsorption condition that described the favorable adsorption condition at low temperature. From Table 2. it clear that the ΔS values were negative in all adsorbent condition. It is indicated that the since the adsorption process, there is no significant changes occurred in the surface of the adsorbent [9]. These result also presented that the ΔH values in all adsorbent condition gave a negative value. The enthalpy change in all adsorption condition lies in range between -9 to -4 kJ mol^{-1}. That phenomenon indicating that the adsorption process was chemisorption [17]. The ΔH value at adsorption process with activated bentonite at 500 °C has the higher value at -9,75 kJ mol^{-1}. This value indicating that the force attraction between the dye and adsorbent surface was increased. That phenomenon is due to the rise of the entropy change.

TABLE 2. Thermodynamic adsorption parameter

Adsorbent	R^2	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1})	- ΔG^o (kJ mol^{-1})		
				30 °C	50 °C	70 °C
Natural Bentonite	0.9972	-9.014	-0.065	8.362	12.007	13.308
Activated Bentonite (300 °C)	0.9725	-7.780	-0.048	5.173	7.890	8.861
Activated Bentonite (400 °C)	0.8742	-4.428	-0.044	7.429	9.916	10.805
Activated Bentonite (500 °C)	0.9152	-9.758	-0.065	7.739	11.409	12.720

CONCLUSION

This study presented that natural bentonite and activated bentonite by thermal activation as an abundant and low cost adsorbent material are considerably adequate to remove the congo red dye contaminant in wastewater. The adsorption process was slightly affected by adsorption temperature. The adsorption kinetics of congo red on natural and thermal activated bentonite follow the first-order kinetics of Langmuir-Hinshelwood model. The thermodynamic study has revealed that the adsorption process was exothermic with negative enthalpy value in all adsorbent condition.

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