

## Cr/Al Pillared Bentonite and Its Application on Congo Red and Direct Blue Removal

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**ABSTRACT.** Bentonite was modified through pillarization with metal oxide Cr/Al in 2:1 and 1:2 ratio to obtain larger basal spacing of bentonite-layered structure. Pillarization was conducted via intercalation method at room temperature followed by calcination. The result was characterized by using XRD and FT-IR Spectrophotometer. XRD pattern shown pillarization by Cr/Al 2:1 ratio gave peak at  $2\theta$  5.3° which is correspond to  $d = 16.4 \text{ \AA}$ . At 1:2 Cr/Al ratio, peak appears at  $2\theta$  6.4° that is related to  $d = 13.7 \text{ \AA}$ . FTIR Spectroscopy measurement gave inconclusive result. The Cr/Al pillared bentonite at 2:1 ratio was applied as adsorbent on Congo red and Direct blue dyes. The result indicates the adsorption follows Freundlich isotherm. Adsorption rate for both dyes follows pseudo-second order with rate constant of pillared bentonite higher than natural one. Adsorption isotherm concludes that Freundlich isotherm is favorable compare to Langmuir. Thermodynamic evaluation suggests that isotherm occurs spontaneously in an exothermic process.

**Keywords:** Bentonite, pillarization, Cr/Al, Congo red, Direct blue.

### INTRODUCTION

One of the most abundant clays mineral naturally occurred is bentonite (Abderrazek, Najoua & Srasra, 2016). Bentonite can be classified as smectite clay having layered structure consists of tetrahedral and octahedral sheets of metal oxide. It is known as montmorillonite, and comprises the bentonite up to 85% (Abdullahi & Audu, 2017). Bentonite clay has general formula  $[(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20}\cdot n\text{H}_2\text{O}]$ , which formed silica and alumina (Hao et al., 2014). Layered material within bentonite structure is separated by only a small gap filled with exchangeable cations such  $\text{Na}^+$ ,  $\text{K}^+$  etc. In order to use bentonite as an adsorbent or catalyst, the gap between layers in bentonite needed to enlarge hence it can be used effectively (Goodarzi, Najafi, & Shekary, 2016). Exchangeable cations within gap between layers can be replaced by larger cations to make the bentonite structure more open, this procedure known as pillarization which has additional purposes i.e. increase strength of the layered structure when it use in elevated temperature (Widjaya, Juwono, & Rinaldi, 2017).

Metal oxide of Cr and Al combination has been used in bentonite pillarization. Bentonite clay has an overall neutral charge; it has an excess negative charge on its lattice and is characterized by a three-layer structure with two silicate layers enveloping an aluminate layer. This arises from the partial replacement of tetravalent silica with trivalent

aluminum that leads to the replacement of trivalent aluminum with divalent calcium. Since opposite charges attract, the negatively charged surface lattice of the bentonite clay may have an affinity for cationic dye (Adeyemo, Adeoye, & Bello, 2017). The pillared bentonite result was used in Congo red and Direct blue removal. Congo red is an azo type dye (R-N=N-R), it is toxic and hardly degraded in nature due to complex molecular structure which consists of aromatic rings (Unuabonah, Adebawale & Dawodu, 2008). Direct blue is an azo methane type dye (-C=N-) which also has aromatic bonds within its molecular structure (Ventura-camargo & Marin-morales, 2013). Here, we reported pillarization of bentonite using combine metal oxide of Cr and Al via intercalation method. The Cr/Al pillared bentonite as well as pristine bentonite were characterized by using XRD and FTIR and were applied on Congo red and Direct blue adsorption.

### EXPERIMENTAL SECTION

Materials used in this research were analytical grade i.e. HCl, NaOH,  $\text{H}_2\text{SO}_4$ ,  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (purchased from Merck Millipore), Congo red and Direct blue dyes were purchased from local supplier. Controlled bentonite was obtained from Lahat. 50 g bentonite was activated chemically by using 250 mL  $\text{H}_2\text{SO}_4$  2 M and 500 mL aquades. Activation was conducted by stirring for 16 hours. The mixture was filtrated and washed in

distilled water until its filtrate was neutralized. Solid was heated and grounded to obtain 200 mesh and then was characterized by using XRD and FTIR.

Pillarization was carried out by mixing pillaring solution (prepared from 40 mL  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  0.5 M and 80 mL  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  0.5 M in 2:1 and 1:2 ratio) with 12 g activated bentonite. The mixture was stirred at room temperature for 24 hours followed by filtered and dried in open air for another 24 hours. The resulting solid was calcined at 400 °C for 2 hours in Muffle Furnace. Pillared bentonite was characterized by using XRD and FTIR. Point of zero charge was measured in various solution pH adjusted by using acid and base solution.

### Congo red and Direct blue Adsorption Experiments

Congo red (CR) and Direct blue (DB) adsorption experiments were conducted in batch reactor. Adsorption was carried out in various pH (1-9), adsorbent weight (0.01; 0.03; 0.1; 0.2 and 0.3 g), adsorption time (5, 10, 15, 20, 30, 45 and 60 minutes), CR and DB initial concentration and temperature (30, 50 and 70 °C). The adsorption procedure is as followed, 0.05 g of Cr/Al pillared bentonite was mixed with 50 mL dyes (CR and DB) at various concentration. The pH of mixtures were set at particular condition. Horizontal shaker was used to homogenize adsorption mixtures for pre-determined period of time. The mixture finally was filtered and the remaining dyes were measured by using spectroscopy UV-Visible

The concentration of remaining dyes after adsorption process by using Cr/Al pillared bentonite was measured. The calculation was assisted by calibration curve of dye at well-established concentration plotted against intensity measured by Spectroscopy UV-Visible. The effect of various parameters were evaluated against Cr/Al pillared bentonite performance on Congo red and direct blue removal from aqueous medium. Parameters to be evaluated as mentioned above were: solution pH, adsorbent weight, adsorption time, dyes initial concentration and temperature.

Adsorption isotherm was evaluated according to two approaches, Langmuir isotherm and Freundlich isotherm. Langmuir isotherm was calculated by using the following formula:

$$\ln q_e = \ln K_f - \ln C_e \quad (1)$$

Where:  $q_e$  is adsorbate amount (mg/g),  $K_f$  is equilibrium constant (L/g),  $C_e$  is equilibrium concentration (mg/g).

Freundlich isotherm was also calculated compared with the Langmuir, which is the best followed refereeing by correlation coefficient obtained. The Freundlich was calculated by using formula as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (2)$$

Where:  $q_e$  is adsorbate amount (mg/g),  $K_L$  is

equilibrium constant (L/g),  $C_e$  is equilibrium concentration (mg/g),  $q_m$  is adsorption maximum capacity (mg/g).

Adsorption rate was assessed according to adsorption kinetic data which was presumed to follows one of two approaches used namely pseudo first order and pseudo second order rate. The equation used in these approaches were:

$$\log (Q_e - Q_t) = \log Q_e - \left( \frac{k_1}{2.303} \right) t \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

Where:  $Q_e$  is adsorption capacity (mg/g),  $Q_t$  is adsorption capacity at  $t$  (mg/g),  $t$  is adsorption time (minute),  $k_1$  is adsorption rate constant pseudo 1<sup>st</sup> order,  $k_2$  is adsorption rate constant pseudo 2<sup>nd</sup> order Thermodynamic assessment was carried out based on the following equation:

$$\ln \frac{Q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

The change of Gibbs free energy, enthalpy as well as entropy was calculated according to general equation:

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

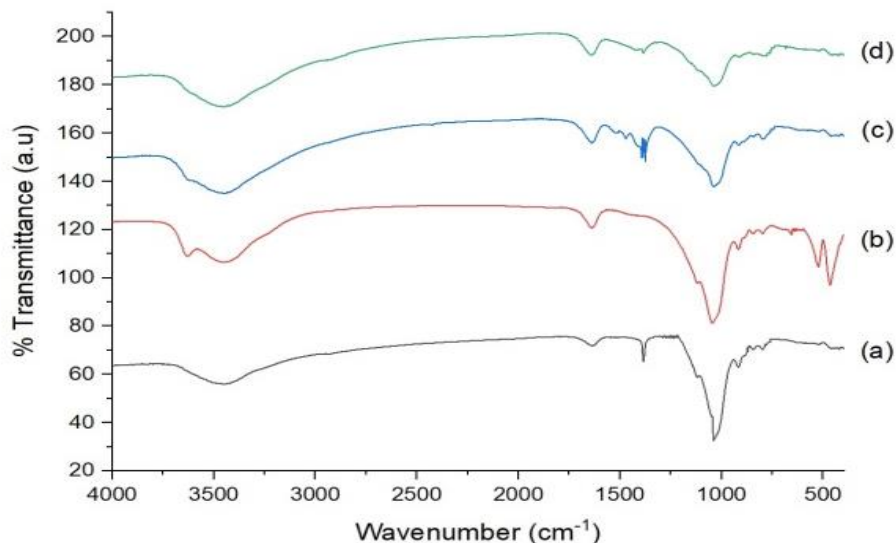
Where:  $\frac{Q_e}{C_e}$  is adsorbate distribution coefficient,  $\Delta H$  is Enthalpy (kJ/mole),  $\Delta S$  is Entropy (J/mole),  $\Delta G$  is Gibbs free energy (kJ/mole),  $R$  is gas constant,  $T$  is Temperature,  $E$  is adsorption energy (kJ/mole) equal to  $\Delta G$

## RESULTS AND DISCUSSION

Preliminary characterization of controlled bentonite by using FTIR spectroscopy indicates stretching vibration of Si-O-Si, Al-O-Al, bending vibration of H-O-H as confirmed by peaks at wavenumber 1033, 910, 1635 and 532  $\text{cm}^{-1}$  whereas stretching vibration of Si-O-Al and O-H were indicated at 686 and 3448  $\text{cm}^{-1}$  (Faghihian & Mohammadi, 2014).

As the bentonite was pillared, some peaks are diminish while other is pronounced as depicted at **Figure 1**. The figure also shows FTIR spectra of Cr/Al pillared bentonite after being used to adsorb Congo red and Direct blue. Peak shift is slightly detected on stretching vibration of Si-O-Si as shown on **Figure 1**. The initial peak Si-O-Si at 1002  $\text{cm}^{-1}$  is shifted to 1040  $\text{cm}^{-1}$  after being used to adsorb Congo red.

The FTIR spectra of Cr/Al pillared bentonite after being used to adsorb dyes however, reveals no confirmation of functional group which belong to dyes adsorbed onto the clay. Qualitatively, the adsorption of dyes by Cr/Al pillared bentonite can be seen from the reducing of color intensity of dye solution used. The existence of azo dyes functional groups cannot be detected hence cannot be ascertained.



**Figure 1.** FTIR spectra: (a) Controlled bentonite, (b) Cr/Al pillared bentonite, (c) after used to adsorb Congo red, (d) after used to adsorb Direct blue

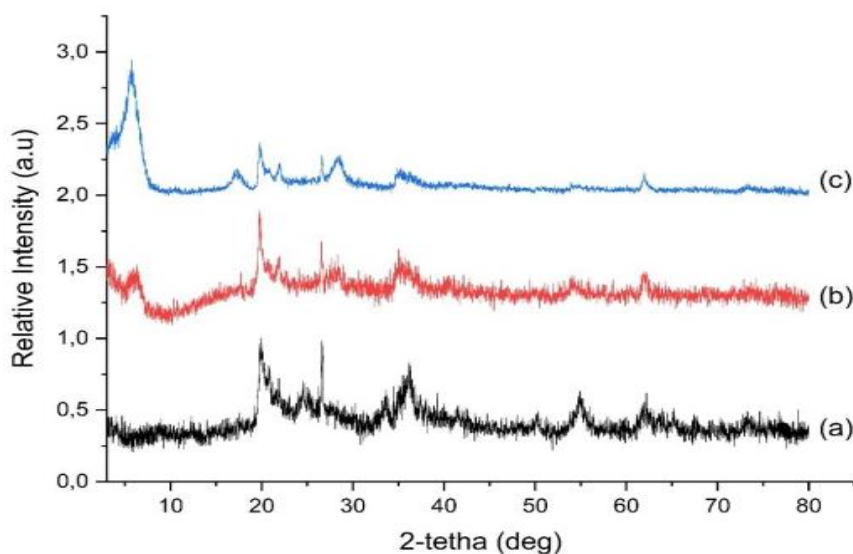
#### XRD Pattern of Natural Bentonite and Cr/Al Pillared Bentonite

Pillarization of bentonite by Cr and Al oxide caused increase of basal spacing between layers on the clay. The shift of  $2\theta$  at specific angle can be used to determine whether pillarization succeed to increase the layer distance or not. **Figure 2** displays XRD pattern of bentonite pristine and after being pillared by Cr/Al at 1:2 and 2:1 ratio of Cr to Al.

Compare to controlled bentonite (**Figure 2c**), the Cr/Al pillared bentonite at 2:1 ratio (**Figure 2b**) shows  $2\theta$  alteration at  $2^\circ$  to  $5^\circ$  whereas Cr/Al pillared bentonite at 1:2 ratio (**Figure 2a**) shows no peak being altered. From the calculation by using Bragg law indicates the basal spacing of pillared bentonite with ratio 2:1 is increased to  $16.4 \text{ \AA}$  from

the original value as shown by controlled bentonite by  $13.7 \text{ \AA}$ . The 2:1 Cr/Al ratio appears to be able to replace the exchangeable cations between layers of bentonite. The combine cations upon calcination was turned into metal oxide which then enlarge the distance between layers. As the conclusion, we decided to use 2:1 Cr/Al pillared bentonite as the material for the next step of experiment.

The oxides of Cr and Al, which was intercalated into bentonite matrix, should had gave peaks on XRD pattern. The small amount of Cr and Al compare to bentonite weight however, were not able to be detected by XRD instrument. Weight of metal oxide below 10% had been reported cannot be detected by XRD to appear as distinct peaks.



**Figure 2.** XRD pattern of (a) Cr/Al pillared bentonite 1:2 ratio (b) Cr/Al pillared bentonite 2:1 ratio and (c) controlled bentonite.

**Point of Zero Charge Controlled bentonite and Cr/Al Pillared Bentonite**

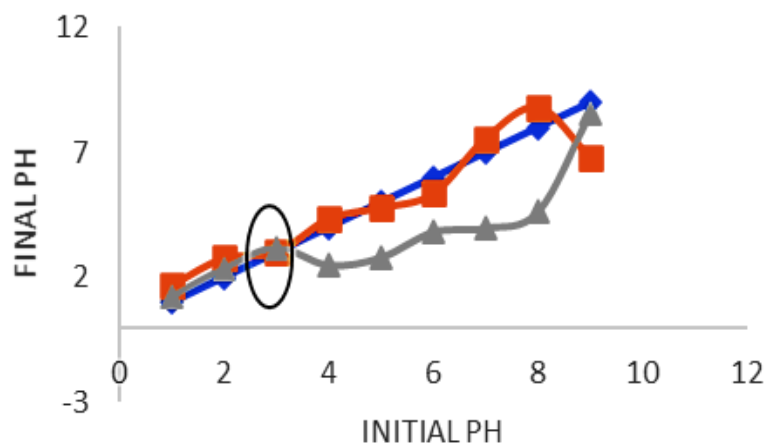
Surface of bentonite has been reported to have negative charge due to hydroxyl groups attached on the silica-alumina layers. Upon solvation, bentonite formed colloidal solution having stabilization depend on solution pH (Niriella & Carnahan, 2006). The charge balance of bentonite surface also plays important role on ions adsorption ability of the material. Point of zero charge (pzc) resemble the condition at which bentonite surface has zero charge due to pH condition adjusted by acid and base addition. **Figure 3** depicted a pH effect on surface charge of bentonite by adding acid or base into the mixture.

From the Figure 3 shows that the pH 3 state equal so that the surface is neutrally charged. At pH > 3 the pillared bentonite was negatively charged so that it is easier to adsorb the Direct Blue dyes since the DB has cation charge, whereas at pH <3 the pillared bentonite was positively charged so that it easier to

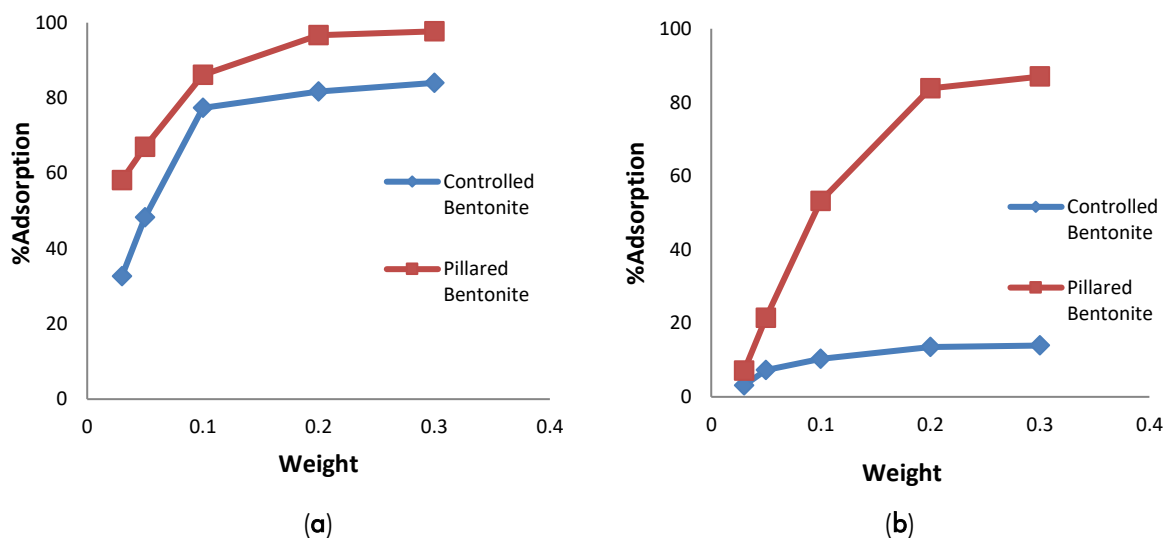
attract the Congo Red dyes since CR has anion charge. The activated carbon has a pH pzc 6 that is bigger than composite. According to Akpomie and Dawodu (2015) bentonite at low pH binds H<sup>+</sup> ions on its surface and creates positive charge. In this condition, bentonite tends to attract anions while at high pH it adsorbed cations due to negative charge originally exist on its surface. The pzc give information on how bentonite surface behave in different pH condition.

**The Effect of Adsorbent Weight on Dyes Adsorption**

Adsorption amount appears to be proportional to the amount adsorbent used but this can be tricky since adsorbent might form aggregate and reduce its effective surface. Adsorbent also has certain amount of adsorbate it can adsorbed known as adsorption capacity. It is an intrinsic property hence its value does not depend of the amount of substance. **Figure 4** show the effect of adsorbent weight to the amount of adsorption of Congo red and Direct blue dye.



**Figure 3.** The pzc pH of controlled bentonite and Cr/Al pillared bentonite



**Figure 4.** The effect of adsorbent weight for (a) Congo red and (b) Direct blue

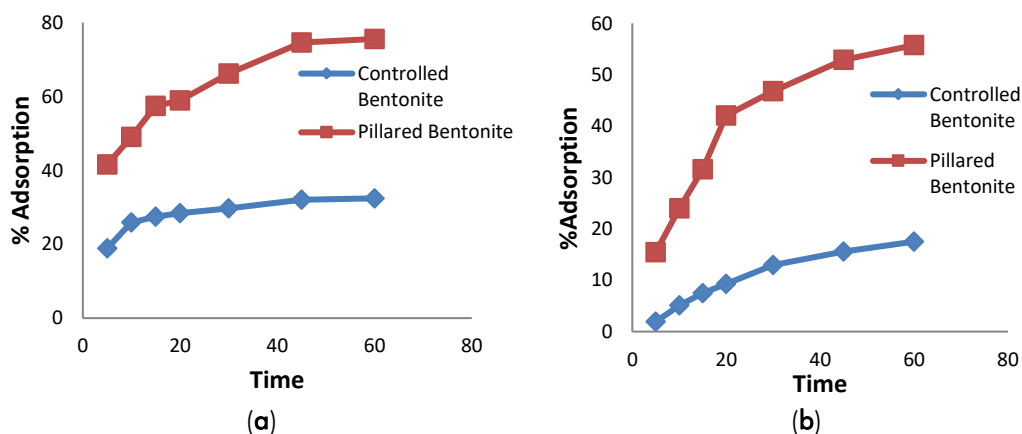
**Figure 4a** shows that adsorption of Congo red for both type of bentonite was similar. The pillarization process provide a larger basal spacing on the treated bentonite therewith-creating surface on the material. The figure however, shows that both natural and pillared adsorbents have similar trend and the extent of adsorption at almost same level. Direct blue adsorption reveals a distinct difference of adsorption amount as shown on **Figure 4b**. Direct blue adsorption by Cr/Al pillared bentonite result in larger amount in comparison with controlled bentonite. The molecular structure of Congo red and Direct blue although represent azo dye's type but has different complexation property in aqueous environment. Cr/Al pillared bentonite shows superior adsorption capacity as a result of increase distance between layers due to intercalation of Cr/Al. This shows that the more controlled bentonite and pillared bentonite, the more active side of the bentonite will be so that it will easily absorb the dye (Chinoune, Bentaleb, Boubberka, Nadim, & Maschke, 2016). In contrast to congo red, direct blue dyes absorbed by controlled bentonite did not show significant results. This is because controlled bentonite and direct blue both have a negative charge so that direct blue dye is difficult to be absorbed by controlled bentonite.

**The Effect of Adsorption Time on Congo red and Direct blue Adsorption**

Solid-liquid adsorption process certainly need more time to achieve equilibrium compare to gas-solid adsorption due to several factors. Solvent

molecule must take into account that provide competing process between the actual adsorbate. Large molecule aimed to be adsorbed also must has molecular orientation in a proper direction to enter pore of the adsorbent. The average contact time of dyes being adsorbed to achieve equilibrium is up to 60 minutes as can be seen on **Figure 5**. Higher adsorption percentage was obtained at the same contact time for Congo red compare to Direct blue. Apparently, Congo red is able to be adsorbed by Cr/Al pillared bentonite in a higher capacity and adsorption rate. The reason for this difference still need further evaluation, but the nature of dye molecule in an aqueous solution might be determining factor. Adsorption by controlled bentonite in both dyes sample has low rate in addition to low capacity. Neither Congo red nor Direct blue were adsorbed more than 40% at the same given time on controlled bentonite. Pillarization process in this case is able to enhance the adsorption capacity of controlled bentonite particularly when it used for dye adsorption. The results agree with previous studies, showing that pillarization of bentonite increases the removal of pollutants (Fosso-Kankeu, Waanders, & Fourie, 2016).

Adsorption rate calculation by using two different approaches i.e. pseudo-first order and pseudo-second order both confirmed that Cr/Al pillared bentonite has bigger rate constant than natural one as presented in **Table 1**.



**Figure 5.** The effect of adsorbent time for (a) Congo red and (b) Direct blue

**Table 1.** Adsorption rate of Congo red and Direct blue on natural (control) and Cr/Al pillared bentonite

	Pseudo-first-order				Pseudo-second-order			
	$Q_{e\ exp}$	$Q_e$	$K_1$	$R^2$	$Q_{e\ exp}$	$Q_e$	$K_2$	$R^2$
CR (Controlled)	32.4085	18.2999	0.0787	0.9254	32.4085	34.5391	0.0072	0.9993
CR (Pillared)	75.5398	67.3363	0.0841	0.9216	75.5398	84.0039	0.0017	0.9964
DB (Controlled)	18.5069	20.8629	0.0414	0.9875	18.5069	36.3155	0.0004	0.9932
DB (Pillared)	55.7386	59.7643	0.0665	0.9904	55.7386	74.6634	0.0007	0.9907

As seen in **Table 1**, the pseudo-second order has higher value of correlation coefficient for both Congo red and Direct blue adsorption. This linearity requirement suggest that pseudo-second order provide best fit for adsorption of Congo red and Direct blue. This phenomenon was similar to another researcher (Biglari et al, 2018). Higher order of reaction rate means there are more concentration exponents that affects the overall rate as well as reaction species involved. This approach used an observable parameter (solute initial concentration) rather than theoretical parameters such as reaction temperature, solution pH, adsorbent particle size and dose and the nature of solute adsorbate.

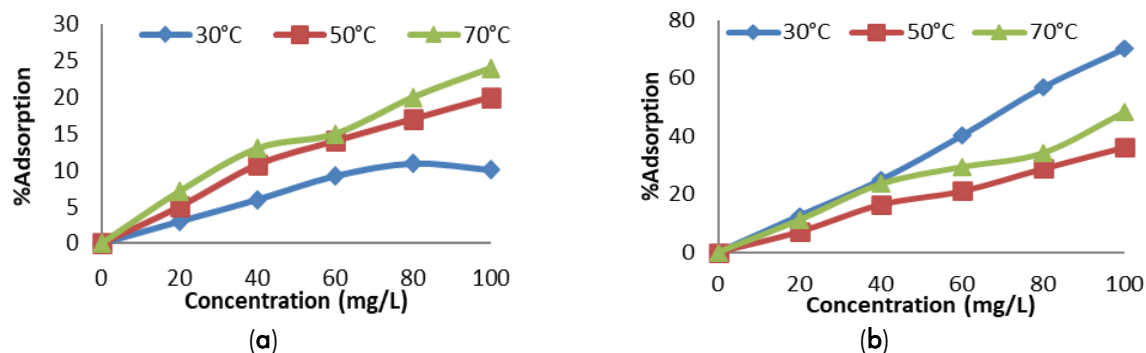
### The Effect of Temperature and Dye Initial Concentration on the Adsorption of Congo Red and Direct blue

At elevated temperature, solute adsorbate provide more thermal energy, which make particle motion, is more active. The probability of particle collision is increased hence the adsorption most likely happen. **Figure 6** depicted similar tendency at which adsorption number increase as the temperature raised. Cr/Al pillared bentonite as shown on **Figure 6b** has higher adsorption percentage than controlled bentonite (**Figure 6a**) at all temperature conducted. At larger surface area available after being pillared, bentonite adsorbed more solute compare to natural

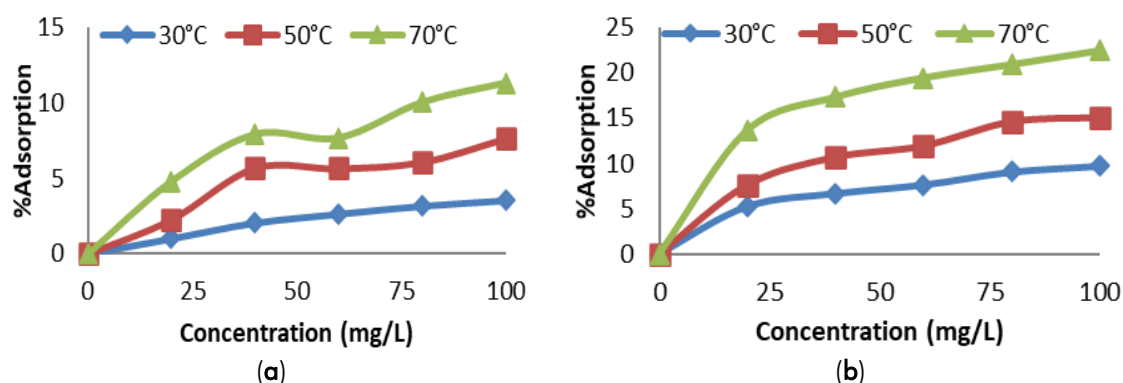
one. Initial concentration of 20 mg/L seems to be the optimum condition of Congo red adsorption by both adsorbents. Solute adsorbate at higher concentration would increase the amount of adsorption as long as there are surface sites available. At limited capacity of adsorbent, initial concentration cannot gives contribution as expected due to surface saturation by solute being adsorbed.

Similarly, Cr/Al pillared bentonite provide more adsorption of Direct blue than controlled bentonite. It is also has optimum initial concentration at same amount i.e. 20 mg/L. The equilibrium condition of Direct blue adsorption on controlled bentonite nevertheless as can be seen on the figure occurs at amount of adsorption in a significant difference.

**Figure 7** show the effect of initial concentration and temperature on the adsorption of Direct blue by using controlled and Cr/Al pillared bentonite. The temperature has great effect on Direct blue adsorption by Cr/Al pillared bentonite. According to **Figure 7** it can be estimated that adsorption at 70 °C occurs almost three times adsorption at 30 °C. The final condition i.e. equilibrium nevertheless occurs in nearly same percent of adsorption. The nature of Direct blue solute might as well affects the adsorption trend observed on both natural and Cr/Al pillared bentonite.



**Figure 6.** The effect of adsorbent concentration on Congo red adsorption amount for (a) controlled bentonite and (b) pillared bentonite



**Figure 7.** The effect of adsorbent concentration on Direct blue adsorption amount for (a) controlled bentonite and (b) pillared bentonite

**Table 2.** Freundlich approach of Congo red and Direct blue adsorption

Temp. (°C)	Parameter	Controlled Bentonite	Pillared Bentonite
30	$K_F$	0.3609	1.0715
	$1/n$	0.7834	0.7625
	$R^2$	0.9231	0.9765
50	$K_F$	0.6179	4.1989
	$1/n$	0.8060	0.5048
	$R^2$	0.9738	0.9903
70	$K_F$	1.3741	4.4364
	$1/n$	0.6537	0.5701
	$R^2$	0.9775	0.9509

**Table 3.** Langmuir approach of Congo red and Direct blue adsorption

Temp. (°C)	Parameter	Controlled Bentonite	Pillared Bentonite
30	$K_L$	0.0098	0.0102
	$Q_m$	23.834	68.273
	$R^2$	0.6737	0.8598
50	$K_L$	0.0075	0.0343
	$Q_m$	53.781	48.737
	$R^2$	0.8602	0.9396
70	$K_L$	0.0144	0.0324
	$Q_m$	43.449	65.502
	$R^2$	0.8735	0.8132

Generally, adsorption is an exothermic process especially when gaseous adsorbate stuck to solid adsorbent. Therefore, as temperature increase, the adsorption tends to decrease because gas has more energy to overcome surface adsorbent attraction. In solid-solution system however, adsorption can be either exothermic or endothermic, depends on what factor affecting and take role as determining aspect. According to **Figure 7**, the result is better than finding by Murcia-Salvador et al. (2019) about adsorption of direct blue and Fosso-Kankeu et al. (2016) about adsorption of congo red.

By using approximation based on Langmuir and Freundlich approach, we will be able to determine whether the adsorption occurred in chemically manner or physically manner. The data calculation base on Langmuir and Freundlich approach are represented on **Table 2 and Table 3** for Congo red and Direct blue adsorption.

Linearity evaluation suggest that Freundlich approach has higher correlation compare to Langmuir approach. The  $R^2$  value for Freundlich isotherm has value up to 0.9 while Langmuir isotherm mostly has  $R^2$  value below 0.9. **Table 2** reveals for controlled bentonite, adsorption isotherm of Congo red is favorable at 50 °C whereas Cr/Al pillared bentonite is favorable at lower temperature i.e. 30 °C as indicates by bigger  $1/n$  value. Freundlich isotherm

suggest that both adsorbents tend to for multilayer of adsorbate on surface of adsorbent. The probable interaction might include physical force (physisorption). The adsorption of Direct blue on controlled bentonite best fits to the Freundlich approach especially at higher temperature having  $R^2$  up to 0.91 same as adsorption by Cr/Al pillared bentonite also at 70 °C. The nature of solute adsorbate affects the adsorption mechanism in different way as it was being adsorbed on natural and pillared bentonite.

Thermodynamic evaluation by using adsorption isotherm data was able to obtain several parameters such as  $\Delta S$ ,  $\Delta H$  and  $E$ . Both adsorbents show similar trend on the increase amount of solute adsorbed when initial concentration and adsorption temperature was elevated. Here we reported only for Cr/Al pillared bentonite thermodynamic calculation for Congo red and Direct blue adsorption as shown on **Table 4 and 5**.

**Table 4** shows that Congo red adsorption on Cr/Al pillared bentonite is an exothermic process as indicated by negative value of  $\Delta H$  and occurs spontaneously ( $\Delta S > 0$ ). The equilibrium amount of solute being adsorbed on the adsorbent is increased when initial concentration and temperature was setup at higher value. Surface area of Cr/Al pillared bentonite proved to be available for adsorption

process at larger initial concentration and higher adsorption temperature. Although the adsorption process occurs spontaneously, its spontaneity value is decreased when solute was adsorbed at larger amount. At this condition, adsorption energy required a bigger value to overcome the repulsion force from greater number of solute being adsorbed. Similar tendency can be seen also occurs on Direct blue adsorption by Cr/Al pillared bentonite. **Table 5** displays the thermodynamic parameters calculated for this adsorption process. Adsorption generally

occurs spontaneously indicated by positive value of entropy change. The enthalpy value however, can have either positive or negative value depends on the nature of solute and adsorbent surface and pores. Several interactions can be contributed on adsorption process which affects enthalpy value of the process. Some interaction might need energy while others might release it. It is possible for solid-liquid adsorption to occur exothermically or endothermically but in our case, both natural and pillared bentonite adsorbed solute adsorbate exothermically.

**Table 4.** Thermodynamic parameters of Congo red adsorption by Cr/Al pillared bentonite

Conc. (mg/L)	T (K)	Q <sub>e</sub> (mg.g <sup>-1</sup> )	ΔS (J/mole)	ΔH (kJ/mole)	E (kJ/mole)
20	303	0.5456	85.651	-34.609	60.561
	323	0.7039			62.274
	343	1.3104			63.987
40	303	13.143	69.331	-22.979	43.986
	323	16.410			45.373
	343	23.544			46.759
60	303	17.896	50.039	-17.468	32.629
	323	21.073			33.630
	343	29.415			34.631
80	303	19.217	52.636	-18.756	34.704
	323	28.831			35.757
	343	34.275			36.809
100	303	21.957	75.406	-25.992	48.840
	323	36.204			50.348
	343	48.312			51.856

**Table 5.** Thermodynamic parameters of Direct blue adsorption by Cr/Al pillared bentonite

Conc. (mg/L)	T (K)	Q <sub>e</sub> (mg.g <sup>-1</sup> )	ΔS (J/mole)	ΔH (kJ/mole)	E (kJ/mole)
20	303	0.527	68.068	-29.15	20.654
	323	0.863			22.015
	343	1.063			23.377
40	303	11.696	85.910	-28.38	26.059
	323	16.696			27.777
	343	24.293			29.495
60	303	17.661	89.943	-29.61	27.282
	323	24.940			29.081
	343	37.413			30.879
80	303	25.081	63.215	-21.13	19.175
	323	34.620			20.439
	343	43.885			21.703
100	303	55.739	43.379	-12.63	13.156
	323	61.094			14.024
	343	69.408			14.891



## CONCLUSION

Pillarization of controlled bentonite by combined metal of Cr and Al provide larger surface area due to increase of basal spacing between layers of the material. Optimum ratio of Cr/Al was obtained at 2:1 which increased its spacing from 15.2 to 16.4 Å. The larger surface area of Cr/Al pillared bentonite was proven by the adsorption of Congo red and Direct blue which was able to adsorb 90-100% of solute adsorbate. For the Congo red removal, adsorption rate (k) was found 0.0017 min<sup>-1</sup>. The adsorption capacity up to 48.31 mole/g. The adsorption energy was obtained in positive sign and calculation gave result at 70 °C as 63.98 kJ/mole. The enthalpy value (ΔH) and the entropy (ΔS) is increased with the increasing of concentration. Meanwhile, the adsorption of Direct blue has similar results. The adsorption capacity, the adsorption energy were 0.0007 min<sup>-1</sup>, 69.4 mole/g, respectively. In addition, the enthalpy (ΔH) and the entropy (ΔS) also increase along with increasing concentration. The optimum pH of adsorption was found out at pH 2, at this pH, controlled bentonite adsorbed Congo red as much as 75.15 mg/L and the pillared bentonite adsorbed 88.9 mg/L. The adsorption of Direct blue at similar pH is 39.22 mg/L for controlled bentonite and 89.05 mg/L for pillared bentonite

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