

icocsti 2019

by Muhammad Said

Submission date: 10-Aug-2022 01:39PM (UTC+0700)

Submission ID: 1880926127

File name: 11_M.Said_ICOCSTI_2019.pdf (619.37K)

Word count: 5315

Character count: 27007

Pillarization of Bentonite using Fe³⁺/Ti⁴⁺ and Its Application for Congo Red and Direct Violet Removal

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Keywords: Bentonite, Pillarization, Fe³⁺/Ti⁴⁺, Congo red, Direct Violet, Adsorption.

Abstract: Bentonite was pillarized by using Fe³⁺/Ti⁴⁺ metal oxide ratio 2:1 and 1:2. The pillarization product was characterized by using XRD analysis and FT-IR spectrophotometer. XRD diffractogram showed that the optimal product was obtained at Fe³⁺/Ti⁴⁺ ratio 2:1. At this ratio, basal spacing of bentonite layer is 15 Å while bentonite with ratio 1:2 has basal spacing 12.86 Å. Bentonite 2:1 ratio was applied on Congo red adsorption. The isotherm adsorption was calculated and followed Freundlich model having adsorption rate (k) 0.0008 (min⁻¹) for Congo red and 0.00045 (min⁻¹) for direct violet. The adsorption capacity (q_e) of Congo red at 70 °C is 68 mol/g that larger than 51 mol/g for direct violet. The adsorption energy (E) of Congo red at 70°C is 4.90 kJ/mol also higher than direct violet with 1.01 kJ/mol. The enthalpy (ΔH) and entropy (ΔS) is decreased with increase of Congo red and direct violet concentration. The optimum pH was obtained at 3 whereas the maximum amount of Congo red adsorbed is 90.60 mg/L. Direct violet shows maximum amount of adsorption at pH 4 with 79.61 mg/L.

1 INTRODUCTION

Bentonite is a naturally occurring material with layered structure contains inorganic exchangeable cations (Kaufhold and Dohrmann, 2008). It is also known as clay mineral composed predominantly by montmorillonite ~85% (Martin et al., 2019) with general formula (OH)₄Si₈Al₄O₂₀.nH₂O (Hao et al., 2014). The exchangeable cations contain within layer structure of bentonite in addition to swelling ability made this material suitable for adsorbent and catalyst application (Sahara, 2010).

Natural bentonite has been used in direct application but shows low effectively due to small inter-layer distance and unreliable porosity. (Goodarzi et al., 2016). Efforts must be introduced to enhance natural bentonite quality through various methods such as pillarization. Pillarization involves ions, molecules or compounds insertion in the interlayer of bentonite (Okoye and Obi, 2011). In this research, We used macro-anion of Fe³⁺/Ti⁴⁺. Pillarization result has the advantage of larger distance of inter-layer with a steady or permanent porosity (Cool and Vansant, 1998).

Fe³⁺/Ti⁴⁺ Pillared bentonite can be applied as adsorbent for removal of Congo red and direct violet

dyes. Both dyes has azo group (R-N=N-R) and as typical of synthetic dye, it is toxic and hard to degrade due to its complex chemical structure which contains aromatic rings (Unuabonah et al., 2008). The adsorption process was conducted by using Fe³⁺/Ti⁴⁺ pillared bentonite by means to evaluate the effect of pH, adsorbent weight, adsorption time, initial concentration of dyes and temperature. The kinetics and thermodynamic parameters were also evaluated and calculated based on dyes remaining concentration and amount of adsorbed species measured by spectrophotometer UV-Vis.

Here, we report the change of character between natural bentonite and Fe³⁺/Ti⁴⁺ pillared bentonite (made in 2:1 and 1:2 ratio). Both materials was used to adsorb dyes. This work was aimed to determine functional group changes and to evaluate the successful of bentonite pillarization concluded from data obtained from FTIR spectrophotometer and XR-Diffraction.

2 MATERIALS AND METHODS

2.1 Materials

Chemicals used in this research was analytical grade i.e. hydrochloric acids (HCl), sulphuric acids (H₂SO₄), iron (III) nitrate (Fe(NO₃)₃), sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), sodium chloride (NaCl), titanium (IV) isopropoxyde as well as bentonite, congo red and direct violet dyes and distilled water.

The pillared bentonite was achieved by pillaring chemicals with bentonite. The mixture was stirred for 24 hours and then filtered and dried in oven for the next 24 hours. The pillared bentonite was calcined for 2 hours at 400°C. The product was characterized by using XRD and FTIR.

2.2 Congo red and direct violet dyes Adsorption Experiments

Congo red (CR) and direct violet (DV) 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 DV initial concentration and temperature (30, 50 and 70°C). The adsorption procedure is as followed, certain amount of Fe/Ti pillared bentonite was mixed with 50 mL dyes (CR and DV) at various concentration. The pH of mixtures was 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 effect of various parameters was evaluated against Fe/Ti pillared bentonite performance on CR and DV 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:

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

Where: Q_e = adsorbate amount (mg/g), K_L = equilibrium constant (L/g), C_e = equilibrium concentration (mg/g), Q_m = adsorption maximum capacity (mg/g)

Freundlich isotherm was also calculated to be compared with the Langmuir which one is best followed refereeing by correlation coefficient

obtained. The Freundlich was calculated by using formula as follows:

$$\log Q_e = \log K_f + 1/n \log C_e \quad (2)$$

Where: Q_e = adsorbate amount (mg/g), K_f = equilibrium constant (L/g), C_e = equilibrium concentration (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 equations 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 = adsorbate capacity (amg/g), Q_t = adsorbate capacity at t (mg/g), t = adsorption time (minute), k₁ = adsorption rate constant pseudo 1st, k₂ = adsorption rate constant pseudo 2nd

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: Q_e/C_e = adsorbate distribution coefficient, R = gas constant

3 RESULTS AND DISCUSSION

3.1 Natural Bentonite and Fe³⁺/Ti⁴⁺ Pillared Bentonite Characterization Result from X-Ray Diffraction (XRD)

Diffraction pattern of natural bentonite and Fe³⁺/Ti⁴⁺ pillared bentonite made with different ratio (2:1 and 1:2) is shown on Figure 1. The increase of basal spacing due to pillarization process can be apprehend at 2θ angel 3-10° (Bourai et al., 2017).

Natural bentonite shows characteristic pattern at 6.39, 19.77, 26.68, and 34.96°. The 2θ at 6.3° indicates (001) having interlayer distance 13.8 Å. The exchangeable cations and other ions filled the space between layers of bentonite (Wang et al, 2016).

Figure 1b represents Fe³⁺/Ti⁴⁺ pillared bentonite (made with 2:1 ratio) diffractogram reveals characteristic peaks at 2θ: 5.90; 19.73; 26.51 and

35.04°. The diffraction angel shift at 5.90° resulted in distance enlargement at (001) up to 15Å. The Fe³⁺/Ti⁴⁺ pillared bentonite (1:2 ratio) shows characteristic peaks at 6.87; 19.97; 26.74 and 35.04° indicates basal spacing width of (001) by 12.86 Å. XRD pattern confirmed that natural bentonite has 13.8 Å basal spacing which by pillarization at 2:1 increased to 15 Å.

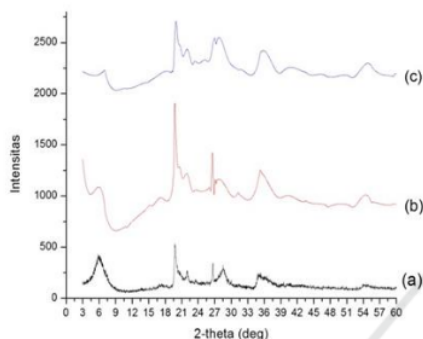


Figure 1: Diffractogram pattern of (a) natural bentonite (b) Fe³⁺/Ti⁴⁺ pillared bentonite made with 2:1 and (c) 1:2 ratio.

Bentonite pillared by Fe³⁺/Ti⁴⁺ at 1:2 ratio on contrary decreased its basal spacing to 12.86 Å. The change of basal spacing can be seen from peak shifting to lower angle. Cations of Fe³⁺ and Ti⁴⁺ entered into interlayer space of bentonite possibly were responsible for the interlayer distance changes (Bourai et al, 2017).

Table 1: Basal spacing of natural bentonite and Fe³⁺/Ti⁴⁺ pillared bentonite as recorded by XRD

Natural Bentonite		Fe ³⁺ /Ti ⁴⁺ Pillared Bentonite 2:1		Fe ³⁺ /Ti ⁴⁺ Pillared Bentonite 1:2	
2θ	d (Å)	2θ	d (Å)	2θ	d (Å)
6.39	13.82	5.90	15	6.87	12.86
19.77	4.48	19.73	4.49	19.97	4.45
26.68	3.33	26.51	3.36	26.74	3.33
34.96	2.56	35.04	2.55	35.04	2.56

Based on XRD diffractogram as summarized on Table 1, optimal pillarization was achieved by 2:1 ratio of Fe³⁺/Ti⁴⁺ cations. The 2:1 ratio Fe³⁺/Ti⁴⁺ pillared bentonite was chosen to be applied on removal of dyes combination of Congo red and direct violet.

3.2 Identification of Dyes Adsorption by Natural and Pillared Bentonite using FT-IR Spectrophotometer

Synthetic dyes has functional groups in its molecular structure which makes them can be identified when it adsorbed onto bentonite by using FTIR spectrophotometer. Figure 2 represents the FTIR spectra for pillared bentonite before and after dyes uptake.

Figure 2a shows typical absorption of natural bentonite at wavenumber 3626 and 910 cm⁻¹ which represent Al-O-(OH)-Al stretching and bending at bentonite octahedral layer. Water molecules presence within bentonite interlayer appears at 3448 and 1635 cm⁻¹ as H-O-H stretching and bending vibration.

Strong absorption band at 1033 cm⁻¹ represents stretching vibration of Si-O-Si in bentonite tetrahedral layer whereas bending vibration appears at 470 cm⁻¹. Al-O-Si bending shows at wavenumber 532 whilst at 686 cm⁻¹ belongs to vibration from feldspar bonding which associated with bentonite (Perelomov, 2016).



Figure 2: FT-IR spectra: (a) natural bentonite, (b) Fe³⁺/Ti⁴⁺ pillared bentonite at 2:1 before and (c) Fe³⁺/Ti⁴⁺ pillared bentonite at 2:1 after congo red adsorption.

Fe³⁺/Ti⁴⁺ pillared bentonite FTIR spectra before adsorption depicted at Figure 2b. Absorption band at 3626 cm⁻¹ represents stretching vibration of Al-O-(OH)-Al at bentonite octahedral layer. Bending vibration of H-O-H detected at wavenumber 1632 cm⁻¹ whereas stretching vibration of Si-O-Si from tetrahedral layer of bentonite appears at 1001 cm⁻¹. Stretching vibration of Al-O and Si-O appears at 796 and 508 cm⁻¹ respectively.

FTIR spectra indicates Fe³⁺/Ti⁴⁺ pillared bentonite after being used for adsorption shows no new peaks from dyes being adsorbed nor peaks change due to adsorption process. The spectra

therefore cannot confirm dyes uptake by pillared bentonite. Figure 2c however still reveals the existence of stretching vibration of Si-O-Si at 999 cm^{-1} and bending vibration of Si-O at 501 cm^{-1} . The dyes adsorbing pillared bentonite particularly Congo red shows peaks at 505-549 cm^{-1} as represent of bending vibration of Al-O-Si.

3.3 Point of Zero Charge (PZC) Analysis

The pH_{pzc} was measured to determine charge property of adsorbent surface i.e. bentonite. This parameter expresses a condition where at certain pH the bentonite surface has no charges. Fabryanty et al, (2007) stated that bentonite will has positive charge at $\text{pH} < \text{pH}_{\text{pzc}}$ and negative charge at $\text{pH} > \text{pH}_{\text{pzc}}$. The analysis result is shown at Figure 3.

Natural bentonite as shown on Figure 3 has pH_{pzc} at pH 3 whilst $\text{Fe}^{3+}/\text{Ti}^{4+}$ pillared bentonite at pH 5. The pH_{pzc} value was difference between adsorbents caused by acidity difference on its surface (Febryanty et al., 2017). Sahara (2010) explained bentonite is an anionic clay or layered materials possesses negative surface charge, hence at pH below its pH_{pzc} the bentonite surface will possesses positive charge due to excess of H^+ ions. At pH above pH_{pzc} , The bentonite surface will possesses negative charge caused by excess OH^- ions presence at it surface. The charge type of bentonite surface affects the adsorption capacity of dyes particularly with opposite charge.

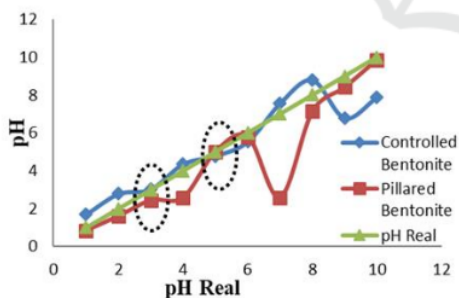


Figure 3: Point zero charge (PZC) of prepared adsorbents

3.4 The Adsorption of Congo red and Direct Violet by using Natural Bentonite and $\text{Fe}^{3+}/\text{Ti}^{4+}$ Pillared Bentonite

3.4.1 The Effect of pH

The effect of pH on Congo red and direct violet adsorption were evaluated at pH 1-10. The remaining dye was determined by using Spectrophotometer UV-Vis at λ_{max} 497 nm. The result can be seen at Figure 4 and 5.

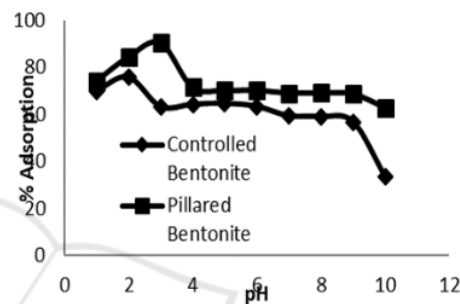


Figure 4: The effect of pH on congo red adsorption by using natural bentonite $\text{Fe}^{3+}/\text{Ti}^{4+}$ pillared bentonite.

Figure 4 appears that $\text{Fe}^{3+}/\text{Ti}^{4+}$ pillared bentonite adsorbed more than natural bentonite (control). The pillared bentonite provides 74-91% adsorption at pH 1-3 but decrease at pH 4-10. Congo red is an anionic dye which is optimally being adsorbed when the adsorbent surface has positive charge (low pH). As the pH becomes more alkaline (pH 4-10). The bentonite surface start to negatively charged due to the excess presence of OH^- ions. At this point, anionic dyes such as Congo red face repulsion from the bentonite surface hence the adsorption number is decreased. This result was supported by the pH_{pzc} value 5 i.e. below this point, Congo red has positive charge which optimally adsorbed this anionic type dyes.

The remaining direct violet after being adsorbed by bentonite was measured by using spectrophotometer UV-Vis at λ_{max} 546 nm. The analysis result is displayed at Figure 5.

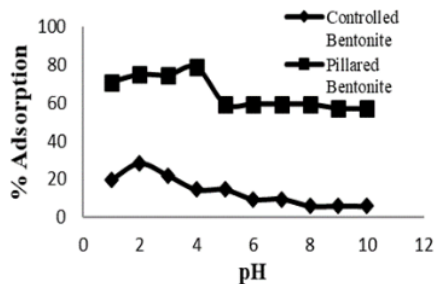


Figure 5: The effect of pH on direct violet adsorption using natural bentonite and Fe³⁺/Ti⁴⁺ pillared bentonite.

The direct violet uptake by Fe³⁺/Ti⁴⁺ pillared bentonite markedly increased at pH 4 by 78%. Above this optimum pH (5-10), the adsorption tends to stable or decrease. Direct violet has similar charge property i.e. anionic dyes hence it shows similar adsorption trends as solution pH changes. Acidic condition makes direct violet more being adsorbed while basic condition less adsorption.

Fe³⁺/Ti⁴⁺ pillared bentonite has p_{H_{zpc}} 5, henceforth the anionic direct violet optimally being adsorbed below this value as the result shown. The positively charged of bentonite surface at this pH able to adsorb more direct violet dyes compare to pH above this value.

3.4.2 The Effect of Adsorbent Weight

The adsorbent weight was varied by 0.03; 0.05; 0.1; 0.2 and 0.3 g at constant concentration of dyes i.e. 100 mg/L. The amount of dyes adsorbed is shown at Figure 6 and 7.

Figure 6 reveals the adsorption of Congo red over natural bentonite and Fe³⁺/Ti⁴⁺ pillared bentonite has similar curve trends but slightly different amount/percentage. The Fe³⁺/Ti⁴⁺ pillared bentonite shows remarkable adsorption to achieve almost 100% Congo red dyes.

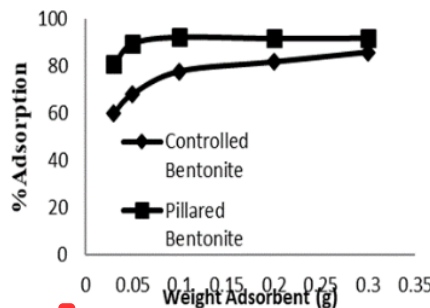


Figure 6: The effect of adsorbent weight on Congo red adsorption

Natural bentonite with original property of its raw material provides 80% Congo red dyes uptake. No significant increase of adsorption at adsorbent weight 0.1 to 0.3 g. It seems that optimum adsorption was achieved at certain ratio of adsorbent to adsorbate rather than to maximize the amount of adsorbent used.

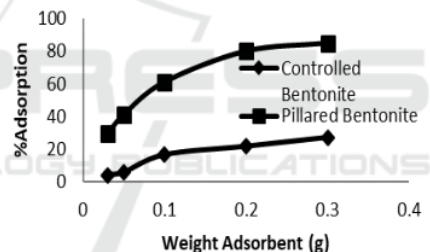


Figure 7: The effect of adsorbent weight on direct violet adsorption over natural and pillared bentonite

Fe³⁺/Ti⁴⁺ pillared bentonite show huge difference of % adsorption compare to natural bentonite when direct violet used as adsorbate. The adsorption shows similar tendency i.e. increase amount of adsorbent caused increase amount of adsorption. The curve slope however indicates the adsorption increment on natural bentonite is low whereas pillared bentonite has steeper slope. It can be concluded that pillared bentonite at the same weight noticeably adsorbed more direct violet than natural bentonite.

The maximum amount of direct violet was adsorbed by pillared bentonite at 0.3 g weight of adsorbent approximately 80%. This result compares to Congo red shows lower % adsorption. The probable cause for this is the structure difference

between both anionic dyes. Congo red has simpler structure with lower number of aromatic molecule whereas direct violet has more aromatic molecules on its molecular structure.

3.4.3 The Effect of Adsorption Time and Its Kinetic Overview

Adsorption of solute adsorbate needs an optimum time to obtain maximum result. Result of adsorption of Congo red and direct violet at various adsorption time is shown on Figure 8 and 9.

Fe³⁺/Ti⁴⁺ pillared bentonite shows its superiority over natural bentonite in both dye adsorption. At the same adsorption time, pillared bentonite provides more dyes uptake than the natural one. The performance of pillared bentonite shows different way between the two dyes adsorbate. Adsorption equilibrium of Congo red over pillared bentonite was achieved at 60 minutes whereas direct violet needs 90 minute to achieve equilibrium.

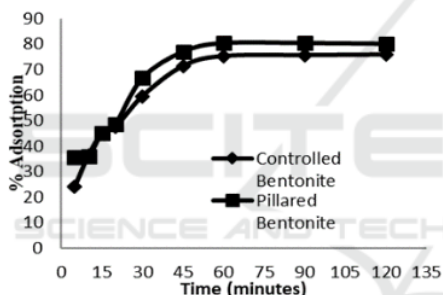


Figure 8: The effect of adsorption time on Congo red removal over natural bentonite and Fe³⁺/Ti⁴⁺ pillared bentonite

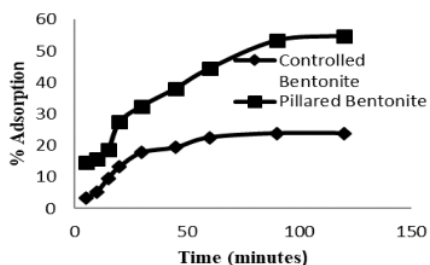


Figure 9: The effect of adsorption time on direct violet removal over natural bentonite and Fe³⁺/Ti⁴⁺ pillared bentonite

Maximum amount of dyes uptake by using pillared bentonite at equilibrium condition is 75-80% for Congo red while direct violet is being adsorbed by 23-53%. No further adsorption occurs after equilibrium due to adsorbent surface is adsorbing at the same rate with desorption process (Bentahar et al, 2017).

Adsorption rate of dyes over natural and pillared bentonite was calculated using time variable of adsorption. The pseudo-first order as well as the pseudo-second order were used as model approach. Several parameters were obtained by this calculation as shown on Table 2.

Table 2: Kinetics model constants of Congo red and direct violet adsorption over natural and pillared bentonite

Kinetic model	Parameter	Dyes type	Control bentonite	Pillared bentonite
Pseudo-first-order	Qe exp	CR	75.7602	80.1301
	Qe		77.0785	88.6103
	K ₁		0.0591	0.0686
	R ²		0.9656	0.9367
Pseudo-second-order	Qe exp	CR	75.7602	80.1301
	Qe		85.8321	90.3501
	K ₁		0.00091	0.0008
	R ²		0.9956	0.9887
Pseudo-first-order	Qe exp	DV	23.8676	54.7647
	Qe		54.2814	60.7603
	K ₁		0.0784	0.0351
	R ²		0.9020	0.9034
Pseudo-second-order	Qe exp	DV	23.8676	54.7647
	Qe		62.8931	68.6696
	K ₁		0.00022	0.00045
	R ²		0.94714	0.9724

Table 2 informs the calculation result based on pseudo-second order approach gave correlation coefficients greater than pseudo-first order for both Congo red and direct violet adsorbate on natural and pillared bentonite. Correlation coefficients of pseudo-second order for Congo red is 0.9956 over natural bentonite and 0.9887 over Fe³⁺/Ti⁴⁺ pillared bentonite. Direct violet shows correlation coefficients 0.9484 over natural bentonite and 0.97014 over Fe³⁺/Ti⁴⁺ pillared bentonite.

These results suggest that the adsorption process is not first order. Pseudo-second order governed according to assumption that rate limiting step of the adsorption might be chemical interaction between adsorbate and adsorbent. This interaction could involve valence forces through electron exchange between anionic molecules and charged surface of bentonite.

3.4.4 The Effect of Concentration and Temperature and Its Thermodynamic Overview

Adsorption of Congo red onto natural bentonite and pillared bentonite was conducted at various concentration and temperatures at pH 3 in a horizontal shaker for 60 minutes. Remaining dyes was measured by using spectrophotometer UV-Vis at λ_{max} 497 nm. The measurement which then was calculated with calibration curve is shown at Figure 10 and 11.

Figure 10 and 11 noticeably point out the similar trend for both adsorbents that is at higher concentration and temperature the amount of dyes adsorbed also raised. The adsorption equilibrium in general was achieved at concentration above 40 mg/L for all temperature in which adsorption conducted. Pillared bentonite although shows similar equilibrium concentration, it has slightly higher adsorption amount compare to natural bentonite. Higher concentration means more frequent collision between molecules of adsorbate and adsorbent whereas higher temperature provides a bigger fraction of molecules with enough energy to performed adsorption process.

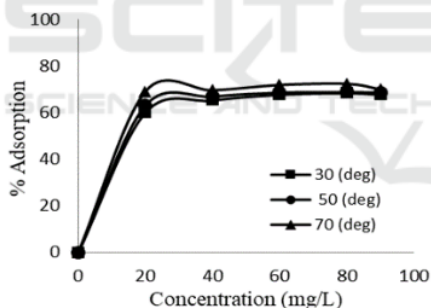


Figure 10: The effect of concentration and temperature on Congo red adsorption over natural bentonite

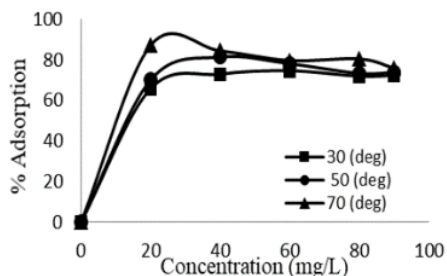


Figure 11: The effect of concentration and temperature on Congo red adsorption over Fe³⁺/Ti⁴⁺ pillared bentonite

Direct violet adsorption was conducted at pH 4 and same duration (60 minutes) in a horizontal shaker. The adsorption process for this adsorbate was measured and calculated as shown on Figure 12 and 13.

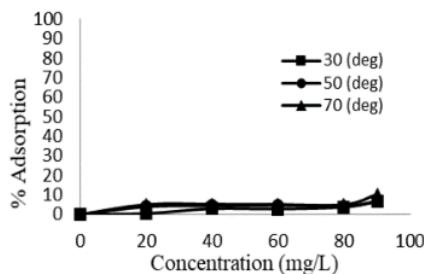


Figure 12: The effect of concentration and temperature on direct violet adsorption onto natural bentonite

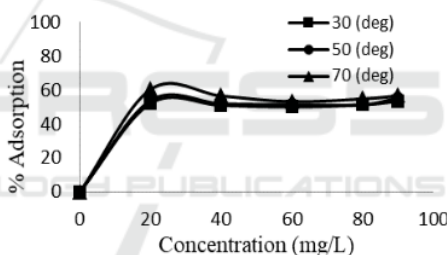


Figure 13: The effect of concentration and temperature on direct violet adsorption onto Fe³⁺/Ti⁴⁺ pillared bentonite

The result of concentration and temperature effect on direct violet adsorption is similar to what was found on Congo red. The difference between natural bentonite and pillared bentonite however, is remarkably high. The increase of adsorption along with concentration and temperature increase on pillared bentonite dwarf the increment on natural bentonite. Equilibrium condition of direct violet adsorption over pillared bentonite was achieved at 60% while natural bentonite can only obtained less than 10%.

At particular temperature, the amount of adsorption reveals an adsorption isotherm. Two models were used in this report i.e. Langmuir and Freundlich. Langmuir isotherm assumed that the adsorption occurred in monolayer fashion provided

that the surface is homogeny. Freundlich isotherm on contrary is a special case of Langmuir approach. According to this theory, the adsorption occurs in a multilayer mode on a heterogeneous surface. The difference between these two models also involved interaction types between adsorbate and adsorbent i.e. chemical or physical. Table 3 and 4 show calculation result for both models along with several constants as stated in its formula.

Table 3: Isotherm data calculated according to Freundlich model

Temp (°C)	Parameter	Dyes	Control bentonite	Pillared bentonite
30	K_f	CR	1.986	5.993
	N		0.783	0.838
	R^2		0.995	0.964
50	K_f		1.208	3.603
	N		0.841	1.063
	R^2		0.997	0.848
70	K_f		1.520	9.687
	N		1.000	1.520
	R^2		0.931	0.985
30	K_f	DV	4.276	1.054
	N		0.373	0.997
	R^2		0.984	0.993
50	K_f		0.019	1.152
	N		0.810	1.010
	R^2		0.957	0.986
70	K_f		0.002	1.150
	N		0.790	1.950
	R^2		0.863	0.986

Table 4: Isotherm data calculated according to Langmuir model

Temp (°C)	Parameter	Dyes	Control bentonite	Pillared bentonite
30	K_L	CR	0.013	0.010
	Q_m		114.9	204.0
	R^2		0.761	0.285
50	K_L		0.009	0.005
	Q_m		175.4	614.9
	R^2		0.746	0.027
70	K_L		0.005	0.064
	Q_m		208.3	119.0
	R^2		0.075	0.947
30	K_L	DV	0.011	0.017
	Q_m		0.374	12.75
	R^2		0.632	0.786
50	K_L		0.004	0.018
	Q_m		9.442	14.02
	R^2		0.522	0.745
70	K_L		0.001	0.013
	Q_m		3.172	33.22
	R^2		0.699	0.890

The effect of temperature on dyes adsorption was tabulated in Table 5 and 6. Based on these data, several thermodynamics parameters were calculated i.e. Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS). The calculation of ΔH and ΔS was carried out by using equation 6 of $1/T$ versus $\ln q_e/c_e$ particularly from its slope and intercept. The value of ΔG was calculated by using equation 7 based on ΔH and ΔS obtained.

Table 5 and 6 displays result of thermodynamic calculation for Congo red adsorption over natural and pillared bentonite. Adsorption capacity (q_e) of both natural bentonite and pillared bentonite was increase proportionally as temperature of adsorption raised.

Table 5: Adsorption energy (E, kJ/mol), entropy (ΔS , kJ/mol), enthalpy (ΔH , kJ/mol) and adsorption capacity (q_e) of Congo red adsorption over natural bentonite at various temperature

Conc. (mg/L)	T (K)	Q_e	ΔS	ΔH	E
20	303	12.01	30.96	8.413	0.96
	323	12.62			1.58
	343	13.80			2.17
40	303	26.10	18.78	4.124	1.56
	323	27.78			1.99
	343	40.60			2.29
60	302	40.60	19.52	4.093	1.82
	323	41.18			2.21
	343	43.07			2.58
80	303	54.70	19.23	3.94	1.88
	323	55.08			2.26
	343	57.80			2.67
90	303	61.02	12.99	2.071	1.86
	323	61.74			2.12
	343	62.89			2.37

Table 6: Adsorption energy (E, kJ/mol), entropy (ΔS , kJ/mol), enthalpy (ΔH , kJ/mol) and adsorption capacity (q_e) of Congo red adsorption over Fe^{3+}/Ti^{4+} pillared bentonite at various temperature

Conc. (mg/L)	T (K)	Q_e	ΔS	ΔH	E
20	303	13.12	93.34	27.02	1.26
	323	14.01			3.12
	343	17.43			4.90
40	303	29.12	96.11	15.48	2.57
	323	32.57			3.76
	343	33.80			4.89
60	302	44.67	30.58	6.537	2.79
	323	46.88			3.34
	343	47.84			3.92
80	303	57.44	41.52	10.26	2.21
	323	58.70			3.04
	343	64.45			3.83

90	303	64.98	22.17	4.332	2.38
	323	66.45			2.82
	343	68.45			3.25

The adsorption capacity of pillared bentonite shows greater value at high concentration of Congo red for all temperature measured. Pillarization treatment was able to increase basal spacing between layers of bentonite hence the capacity of pillared bentonite to adsorb is bigger.

Result of energy calculation exposes that the adsorption energy is positive and increase as temperature rise. Normally, adsorption is an exothermic event hence has negative energy. The unbalance energy at surface was compensated by adsorbing solid adsorbate so it decreases its energy. The situation for adsorption in solution however must take into account solvent contribution. Fontecha-Ca'mara et al. (2006) suspected that the interaction of solvent-adsorbent and solvent-adsorbate could shifts the exothermic mode of adsorption into endothermic one.

The calculated parameters of thermodynamic based on adsorption of direct violet at various temperatures is displayed on Table 7. The adsorption was conducted over Fe³⁺/Ti⁴⁺ pillared bentonite.

Table 7: Adsorption energy (E), entropy (ΔS), enthalpy (ΔH) and adsorption capacity (qe) of direct violet adsorption over Fe³⁺/Ti⁴⁺ pillared bentonite at various temperature

Conc. (mg/L)	T (K)	Q _e	ΔS	ΔH	E
20	303	10.42	24.51	7.306	0.12
	323	10.74			0.61
	343	12.10			1.10
40	303	20.37	16.54	4.988	0.02
	323	20.73			0.35
	343	23.70			0.68
60	302	30.00	9.51	2.847	0.06
	323	30.78			0.27
	343	31.98			0.49
80	303	40.98	10.71	3.183	0.06
	323	41.00			0.27
	343	43.38			0.49
90	303	47.98	11.10	3.023	0.34
	323	49.80			0.56
	343	51.08			0.78

The Gibbs free energy (ΔG) for both Congo red and direct violet according to calculation result is negative which means it occurs spontaneously. Table 7 shows similar trends with previous table. Entropy value obtained nonetheless shows large difference. As temperature increase, so does entropy of both adsorptions. Direct violet appears slightly

smaller entropy compare to Congo red. The complexity of adsorbate structure might hinder the adsorption process due to steric hindrance so it lowers entropy of the process. Enthalpy result is quite similar as Congo red. The type of interaction for adsorption in solution possess was difficulty and not as simple as gas adsorption over solid adsorbent.

4 CONCLUSIONS

Basal spacing of natural bentonite was successfully increased from 13.8 to 15 Å through pillarization using Fe³⁺/Ti⁴⁺ at 2:1 ratio. Quantitatively, spectrophotometer UV-Vis confirmed the dyes removal from decrease of intensity but FTIR spectra gave no peaks indication of the functional groups of corresponding dyes. The optimum adsorption condition is in accordance with pH_{pzc} i.e. higher at pH below pH_{pzc}. Freundlich model for heterogenic surface along with possible chemical interaction is best fit to the process conducted. Thermodynamic of adsorption suggest the process is endothermic and occurred spontaneously.

ACKNOWLEDGEMENTS

The first author want to say thank you to KEMENRISTEKDIKTI for the financial support through Hibah Penelitian Dasar 2019.

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