*Article*

# PILLARIZATION OF LAYER DOUBLE HYDROXIDES (Mg/Al) WITH KEGGIN TYPE K$_4$[a-SiW$_{12}$O$_{40}$].nH$_2$O AND ITS APPLICATION AS ADSORBENT OF PROCION RED DYE

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## ABSTRACT

Pillarization of layered double hydroxides with polyoxometalate K$_4$[α-SiW$_{12}$O$_{40}$]•nH$_2$O at various times i.e. 3, 6, 9, 12, 24, 36 and 48 hours has been done. The pillared product was characterized by FT-IR spectrophotometer and XRD. The optimum pillared layered double hydroxides of polyoxometalate K$_4$[α-SiW$_{12}$O$_{40}$]•nH$_2$O was used as adsorbent of procion red dye. The results of characterization using FT-IR spechtrophotometer is not yet show the optimum pillaration process. The characteritation using XRD the successfully of pillared layered double hydroxides of polyoxometalate K$_4$[α-SiW$_{12}$O$_{40}$]•nH$_2$O showing the existence of diffraction angle 8.5$^o$ with intensity 355. Furthermore, the pillared layered double hydroxides of polyoxometalate K$_4$[α-SiW$_{12}$O$_{40}$]•nH$_2$O with time variation of 12 hours was applied as adsorbent of procion red dye. The results show the adsorption rate was 0.523 min$^{-1}$, the highest of absorption capacity at 70$^o$C was 10.8 mol/g, the higest energy of absorption 70 $^o$C was 125 kJ/mol. The enthalpy (ΔH) and entropy (ΔS), decrease as the increasing consentration of procion red dye.

**Keywords:** layered double hydroxides, polyoxometalate, pillaration, procion red, adsorption

## INTRODUCTION

Layered material based on his being is divided into a layered material found in nature and are synthesized. One example of a layered double hydroxide compounds synthesized double layer. Hydrotalcite is layered material and has general formula [M$^{2+}_{(1-x)}$M$^{3+}$x(OH)$_2$](An-)x/n•nH$_2$O, where M$_2$ and M$_3$ is divalen and trivalen metal cations and An intercultural space is filled by the compound layer hydra (Zhao et al, 2011). Recently, layer double hydroxides are modified by insertion or intercalation between layer using anion (Maruyama et.al, 2016) or macoanion such as polyoxometalate compounds (Asiabi et.al, 2017).

Layered double hydroxides modified with the purpose of enlarging the spacing layer so that it can be effectively used as adsorbent. Modification of layered double hydroxide do with macroanion pillared process. Macroanion compound used was polyoxometalate Keggin type H$_3$[α-PW$_{12}$O$_{40}$].nH$_2$O. The pillared method is used on layered double hydroxide i.e. ion exchange method. Pillarization of macroanion in double layers of hydroxides cause material loss of the anion OH-which located on the layer so that it is expected to enlarge the distance between layers of material layered double hydroxide (Imron and Said, 2017). Polyoxometalates are metal oxygen clusters with various structures, acid base properties, redox properties, and also high solubility depanding on counterions (Misuno, 2013). Polyoxometalate is macroanions, which can be used frequently as intercalant for layer double hydroxides (Omwoma et.al, 2014 ; Hasannia and Yadollahi, 2015).

Layered material is used as a catalyst, adsorbent, sensor, membrane or ion exchange. As adsorbent, a layered material used for aditive adsorption on vegetable oil, as well as its application for the control of contamination of metal ions or organic compounds in the environment. In the industrial field, most of the dyes that have been used will be discharged into the environment. Generally, the dyestuff from the textile industry waste is an organic compound which has an aromatic structure so it is difficult to degrade naturally and certainly not environmentally friendly (Ba-Abbad, et al. 2017).

This research was conducted on the synthesis and characterization of layered double hydroxides, compounds polyoxometalate K$_4$[α-SiW$_{12}$O$_{40}$].nH$_2$O and layered double hydroxides pillared polyoxometalate K$_4$[α-SiW$_{12}$O$_{40}$].nH$_2$O. The successfully pillarization process, material was characterized using FTIR and XRD analyses. Furthermore, pillared material was used as adsorbent of procion red dye. Procion red are toxic and difficult to degraded because it has a complex chemical structure and the presence of aromatic rings. The adsorption process was studied by adsorption time, influence of temperature and concentrations. Concentration of procion red dye was determined using UV-Vis Spectrophotometer (Zhang et al., 2012).

## EXPERIMENTAL SECTION
### Equipments

A set of standard glass tools, magnetic stirrer, thermometer, hotplates, oven, furnace, vacuum, a separator funnel, X-Ray Diffraction (Rigaku Miniflex 600), FT-IR spectrometer (Shimadzu prestige-21) and UV-Vis spectrophotometer (Thermo Scientific Geneysis 20) were used in this experiment.

### Materials

Chemicals to be used in this study such as sodium metasilicate (Na$_2$SiO$_3$), sodium tungstat (Na$_2$WO$_4$), potassium hydroxide (KOH), potassium chloride (KCl), sodium hydroxide (NaOH), sodium carbonate (Na$_2$CO$_3$), magnesium nitrate (Mg(NO$_3$)$_2$), aluminum nitrate (Al(NO$_3$)$_3$), procion red (C$_{15}$H$_{15}$N$_3$O$_2$) and water. Water was supplied from Intergrated Research Laboratory, Sriwijaya University using Puriteâ water filtration systems.

### Procedure
*The synthesis of layered double hydroxides*

Double layer synthesized on hydroxy solution with the concentration of each 50 mL of Mg(NO$_3$)$_2$ 1 M and 20 mL of Al(NO$_3$)$_3$ 1 M added to 250 mL of water and then stirred. pH of solution was adjusted to 10 using NaOH and heated to the temperature of 40 $^o$C. The reaction was kept at a pH value of 10 then added with 20 mL of Na$_2$CO$_3$ 2 M and 10 mL of NaOH 2 M. The solution was heated to 40 $^o$C for 3 hours and left in the oven at a temperature of 70 $^o$C for 40 hours. The product obtained in the form of white suspension washed and dried at room temperature. The products are characterized by XRD powder analysis and FT-IR.

*Synthesis Polyoxometalate K$_4$[a-SiW$_{12}$O$_{40}$]•nH$_2$O*

Synthesis polyoxometalate K$_4$[αSiW$_{12}$O$_{40}$]nH$_2$O synthesized by dissolving sodium metasilicate as many as 11 g in 100 mL of water used as A

solution of as many as 182 g of sodium tungstat dissolved in 300 mL of hot water and a solution of the foundation of the solution b. as much as 165 mL of HCl 4 m added drops demi drops for 5 min with stirring with 300 rpm speed to dissolve deposits of tungstat acid. Then, quickly added solution A into the solution B with the addition of 50 mL followed hydrochloric acid 4 M. The solution is kept for 1 hour at a temperature of 100 °C to the value of pH 5 to 6. As many as 50 mL and 80 mL sodium tungstat hydrochloric acid 4 M is added into the solution quickly. This solution is difiltrasi after it is cooled at room temperature. The solution used to obtain salt or acid $[\alpha\text{-}SiW_{12}O_{40}]^{4+}.nH_2O$. The potassium salt is obtained by adjusting the pH value of the solution at 2 using potassium chloride by as much as 50 g quickly to white from salt deposits acquired potassium form $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ Characterization of compound was done using FT-IR spectroscopy and XRD analysis.

### Preparation of Layered Double Hydroxides Pillared Polyoxometalate $K_4[aSiW_{12}O_{40}]\cdot nH_2O$

The process pillarization of layered double hydroxides by polyoxometalate was conducted using ion exchange method. Reactions is done by making the solution A, polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ as much as 1 g with 50 mL water 100 mL in beaker and solution B, 1 g of double layer in hydroxides was placed into beaker and added 25 mL of 1 M sodium hydroxide. Solution A and solution B was mixied together in one neck round bottom flask with the stirring speed 280 rpm in irrigated conditions gas $N_2$ in order not going direct contact with oxygen in the air while using magnetic stirring in stirer with variations in time. The determination of the variation of time starting from 3, 6, 9, 12, 24, 36, and 48 hours. This suspension is cooled and washed with water and dried at room temperature. Characterization was performed using XRD powder and FT-IR analyses. Application of Pillared Material as Adsorbent of Procion Red

### Effect of Adsorption Time

As much as 2 g pillared material was mixed with 50 mL of procion red with concentration concentration of 25 mg/L. The mixture is then stirred using a horizontal shaker at the appointed time. As control, in a different container as much as 2 grams of non pillared material was applied. Variation of time was 10, 20, 30, 40, 50, 60, 70, 80 and 90 minutes. Procion red and adsorbent was separated by filtration then concentration was measured by using UV-Vis spectrophotometer. Adsorption rate can be calculated using equation (1).

### Effect of Concentration and Temperature Adsorption

Influence of thermodynamic adsorption of procion red adsorption on pillared material was done through a series of experiments by varying the concentration of procion red and temperature. As much as 2 g of adsorbent was mixed with 50 mL of solution of procion red (10, 25, 50, 100 mg/L) while stirring using a horizontal shaker for 1 hour at a temperature that varies (30, 40, 50, 60, 70, and 80 °C). As control, in a different container as much as 2 g of layer double hydroxides was interacted with 50 mL of procion red substances (10, 25, 50, 100 mg/L). The mixture was filtered, then a solution of procion red which has been separated from the adsorbent was measured using a UV-Vis spectrophotometer to know the concentration of residual concentration of procion red. Adsorption

capacity and energy can be calculated using the equation of Langmuir in equations (2) and (3), whereas the entropy and enthalpy adsorption can be calculated using equation (4).

### Data Analysis

The pillared layer double hydroxides was characterized using FT-IR and XRD analyses. Basal spasing value can be obtained based on XRD pattern and it is expected that the pillared material has a layer between layers larger than before the process of pillarization. Pillared material was used as adsorbent of procion red. The adsorption process was studied through kinetic and thermodynamic parameters. The adsorption kinetic was studied by variation of adsorption time and adsorption rate calculated based on Langmuir Heinselwood adsorption equation as follows:

$$\frac{\ln(\frac{C_o}{C})}{C} = k_1\frac{t}{C} + K \tag{1}$$

where:
$C_0$ = the initial concentrations procion red
$C$ = concentrate procionred after time
$t$ = adsorption time
$K$ = adsorption equilibrium constant

The thermodynamic parameters were studied through variations in the concentration of procion red dye and temperature. Adsorption capacity and energy were calculated on the basis of the Langmuir equation as follows:

$$\frac{C}{m} = \frac{1}{bK} + \frac{C}{b} \tag{2}$$

$$E = -RT\ln K \tag{3}$$

where:
$C$ = procion red concentration after adsorption reaches equilibrium
$m$ = mol of procion red adsorbed at 0.5 grams adsorbent
$K$ = equilibrium constant
$b$ = adsorption capacity
$E$ = adsorption energy
$R$ = constant
$T$ = temperature

While to find the value of coefficient of adsorbat distribution used equation as follows:

$$\ln Kd = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4}$$

where:
$Kd$ = coefficient of adsorbate distribution ($qe/Ce$)
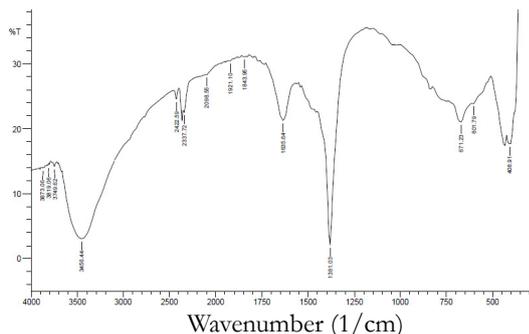$\Delta H$ = enthalpy
$\Delta S$ = entropy
$R$ = constant
$T$ = temperature


Figure 1. FTIR spectra of layer double hydroxides.
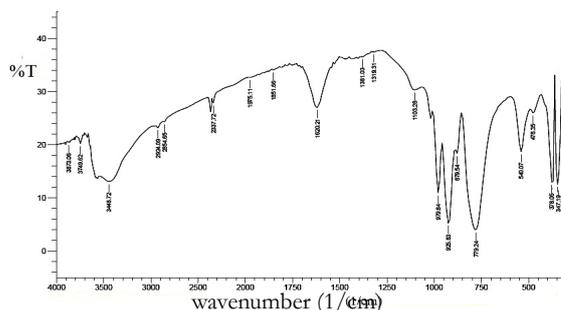

Figure 2. FTIR spectra of polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$.
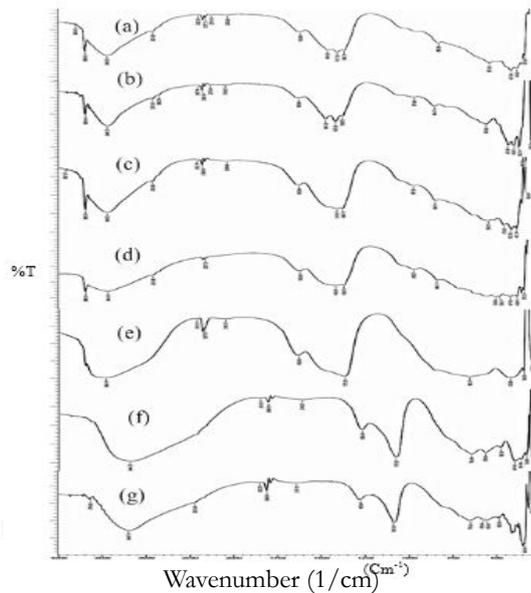
Figure 3. FT-IR spectrum of layered double hydroxides pillared with polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ at 3 hours (a) ,6 hours (b), 9 hours (c), 12 hours (d), 24 hours (e), 36 hours (f) and 48 hours (g).
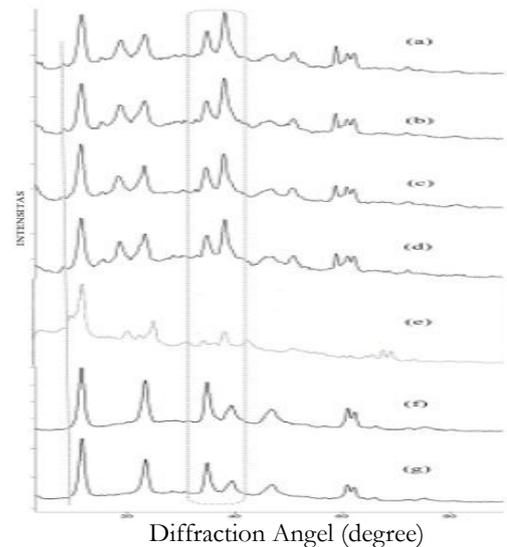


Figure 4. XRD powder patterns of layer double hydroxides pillared with polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ at 3 hours (a), 6 hours (b), 9 hours (c), 12 hours (d), 24 hours (e), 36 hours (f), and 48 hours (g).

## RESULTS AND DISCUSSION

### Characterization of Layer Double Hydroxides and Pillared Layer Double Hydroxides with Polyoxometalate Using FT-IR spectrophotometer

Characterization using FT-IR spectrophotometer resulted in IR spectrum of layer double hydroxides and pillared layer double hydroxides at various temperatures as seen in Figure 1, 2, and 3. It can be seen in Figure 1 that the broad vibration peak between the wavenumber 3800-3300 cm$^{-1}$ is assigned as the vibration of the OH group in the structure of the layer double hydroxides (Zvezdova, 2014). The peak at the wavenumber 1635 cm$^{-1}$ is a bending of OH vibration. The wavenumber at 1381 cm$^{-1}$ is assigned as vibration of stretching of nitrate. Bending vibration of nitrate was also detected at wavenumber 671 cm$^{-1}$. Vibration of Al-O and Mg-O were appeared at wavenumbers 601 cm$^{-1}$ and 408 cm$^{-1}$.

FTIR spectrum of polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ as shown in Figure 2 shows the unique vibration of Si-O at 925.83 cm$^{-1}$. The vibration of W = O was detected at 979.84 cm$^{-1}$. The wavenumber at 879.54 cm$^{-1}$ shows the presence of oxygen W-Oe-W vibrations located on the edge of the polyoxsometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$. Peak at 779.24 cm$^{-1}$ shows the vibration of the W-Oc-W group, where an oxygen atom located at the center of the polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ compound.

The double layer hydroxide was then pillarized with a poloxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ by an aqueous solution wherein the double layer hydroxides was dissolved with NaOH and the polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ was dissolved with water. The weight ratio of layer double hydroxides: polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ was 1: 1. Variation of pillarization time was 3, 6, 9, 12, 24, 36 and 48 hours. The FTIR spectrum

of layer double hydroxides pillared with polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ compound was shown in Figure 3.

FTIR spectrum in Figure 3 showed that almost vibrations are similar at various pillarization times. Pillarization at 3-24 hours give dominant vibration of layer double hydroxides, while pillarization at 36-48 hours resulted almost IR spectrum of polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$. Due to unclear results to determine optimal pillarization process, further characterization was conducted using XRD powder analysis.

### Characterization of Pillared Layer Double Hydroxides Using XRD Powder Analysis.

The XRD powder pattens of layer double hydroxides pillared with polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ at various time was shown in Figure 4. The variation of pilaration time is expected to obtain the best diffraction showing the diffraction of a pillared polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ to layer double hydroxides. Diffraction of polyoxometalate at 6-10°, 15-20°, 22-25°, and 35-40° is emphasized to determine the successful pilarization process Yang et al (2011). On the other hand, diffraction of layer double hydroxides at 10° and 60° is not affected to the pillarization process (Dolidovich and Palkovits, 2015; Shan et.al, 2014). Diffraction at 60° indicating that the presence of anions on the interlayer may be anion nitrate, carbonate, or other anions (Kuang et.al, 2010; Aviles et.al, 2015).

The XRD patterns of pillarization at 3 hours, 6 hours and 9 hours showed there was a peak at an angle of 6-10° with a small intensity. Whereas in the 12 hours pillarization shows characteristic of the pillarized polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ at the diffraction angle 8.5° with
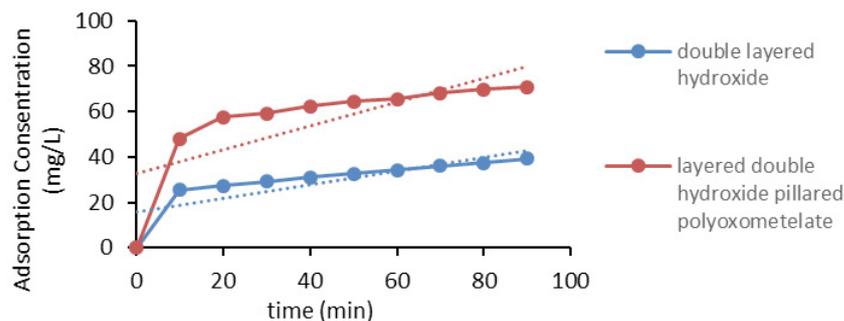


Figure 5. Effect of procion red adsorption time using layer double hydroxide and pillared layer double hydroxides at 12 hours.
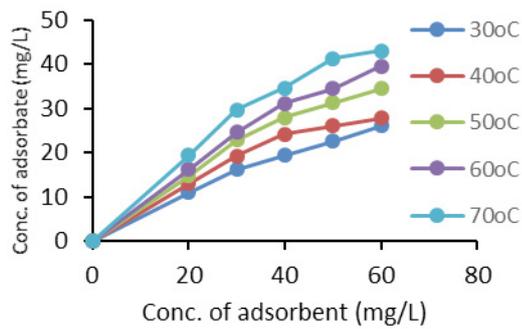
Figure 6. Effect of temperature and concentration of procion red on layer double hydroxides
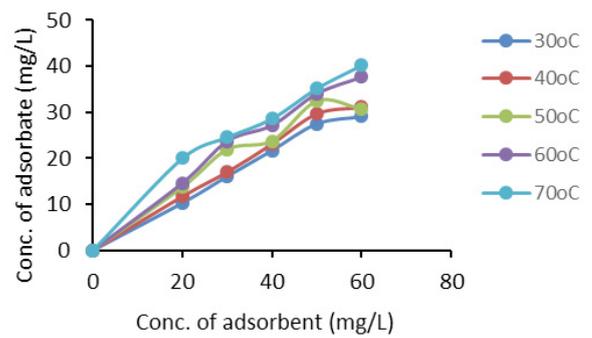


Figure 7. Effect of temperature and concentration of procion red on layer double hydroxides pillared $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$

a intensity of 353.5. Pillarization time at 36 hours and 48 hours showed that there is no peak in the region of 6-10° which is characteristic of the $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$.

From this diffraction data, it can be seen that the 12 hours pillarization time has a diffraction angle of 6, 10, 35 and 40° which is characteristic of layer double hydroxides pillared compound. Other pillarization time at 3 hours, 6 hours, 9 hours, 24 hours, 36 hours and 48 hours does not show any diffraction at 6°. Thus, the optimal pillarization of layer double hydroxides with polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ was achieved at 12 hours. Futher experiment was used layer double hydroxides pillared polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ at 12 hours as adsorbent of procion red dye in aqueous medium.

**Effect of Adsorption Time on Adsorption of Procion Red Using Layer Double Hydroxides and Pillared Material**

Layer double hydroxides pillared with polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ can absorb more adsorbate than double layer hydroxide material at the same time as shown in Figure 5. The optimum absorption occurs in the layer double hydroxides as control which absorbs the procion red dye shown by the blue curve at 50 minutes with absorption of 32.69 ppm from the initial concentration of 60 ppm. On the other hand, adsorption of pillared material reached more than 70 ppm at the same time with layer double hydroxides. The adsorption patterns of layer double hydroxides and pillared material have similar style. Adsorption was slow at initial time and reach equilibrium at around 70 minutes. Layer double hydroxides pillared polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ compound showed the optimum adsorption at 20 minutes with adsorption of 57.45 ppm from initial concentration of 100 ppm. By increasing adsorption time will increase the amount procion red adsorbed. Adsorption was almost constant at 50 minutes. Both physisorption and chemisorption will give similar trend for adsorption by increasing adsorption time (Yu, et al., 2015).

The data was obtained in Table 1 show that layer double hydroxides pillared with $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ has adsorption rate faster than adsorbent before pillarization. Probably due to of layer activity after pillarization can create reactivity of pillared layer double hydroxides.

**Effect of Concentration and Temperature Adsorption of Procion Red Using Layer Double Hydroxides and Pillared Material as Adsorbent.**

Figure 6 and 7 show the effect of temperature and concentration of procion red on layer double hydroxides and pillared material. These results in general shows that the higher the temperature can create the greater

Tabel 1. The adsorption rate of procion red on layer double hydroxides and pillared material.

| Adsorbent | Parameter | |
|---|---|---|
| | $k_1$ (minutes$^{-1}$) | $R^2$ |
| Layer double hydroxides | 0.302 | 0.666 |
| Pillared | 0.523 | 0.569 |

of procio red adsorbed. The greater concentration of procion red also will increase the amount of procion red adsorbed. These phenomena was equal for both layer double hydroxides as adsorbent as shown in Figure 6 and layer double hydroxides pillared $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ as shown in Figure 7.

Figure 6 and 7 shows that there is an adjacent point at the concentration of procion red 10 mg/L and 20 mg/L due to increasing termperature did not increased the adsorption of procion red. The highest adsorption was reached at temperature 70 °C for both layer double hydroxides and pillared material. By increasing concentration of procion red was also increased the adsorption of procion red but at concentration 30 and 50 °C there was a path of adsorption on pillared layer double hydroxides. Probably due to interlayer activity caused unstability of pillared layer double hydroxides.

The adsorption capacity and energy of the procion red dye adsorption on layer double hydroxides and pillared layer double hydroxides were obtained from equation 2-4 and the results are presented in Table 2. In general, adsorption capacity and energy were increased by increasing temperature (Vimoses et al, 2009). In contrast, adsorption capacity of procion red on pillared layer double hydroxides was lower than layer double hydroxides. This phenomena is due to unstable pillared layer double hydroxides toward procion red and also molecular size of procion red is larger than interlayer distance material after pillarization.

The further thermodynamic parameters are enthalpy (ΔH) and entropy (ΔS) of the procion red dye adsorption on layer double hydroxides and pillared material as shown in Table 3. The thermodynamic parameter in Table 3 showed that irregular data. As explained above due to unstable pillared layer double hydroxides toward procion red dye caused enthalpy and entropy can be predicted by increasing temperature and concentration of procion red.

Table 2. Adsorption capacity and energy of procion red dye on layer double hydroxides and pillared material.

| Adsorbent | Temp. (ºC) | b (mg/g) | E (kJ/mol) |
|---|---|---|---|
| Layer double hydroxides | 30 | 28.5 | 9.04 |
| | 40 | 27.02 | 8.69 |
| | 50 | 90.90 | 11.07 |
| | 60 | 111 | 11.13 |
| | 70 | 125 | 10.8 |
| Pillared | 30 | 41.1 | 18.5 |
| | 40 | 46.7 | 15.3 |
| | 50 | 16.8 | 10.9 |
| | 60 | 2.99 | 2.95 |
| | 70 | 16.8 | 1.59 |

Table 3. The enthalpy value ($\Delta H$) and entropy ($\Delta S$) of procion red dye adsorption on layerv double hydroxides and pillared material

| Adsorbent | Co | $R^2$ | $\Delta H$ (kJ/mol) | $\Delta S$ (kJ/mol) |
|---|---|---|---|---|
| Layer double hydroxides | 20 | 0.821 | -5004 | 182.2 |
| | 30 | 0.948 | -3505 | 123.7 |
| | 40 | 0.957 | -2536 | 93 |
| | 50 | 0.948 | -2994 | 107 |
| | 60 | 0.972 | -2260 | 79.79 |
| Pillared | 20 | 0.048 | -4461 | 0.136 |
| | 30 | 0.946 | -2689 | 99.1 |
| | 40 | 0.929 | -1363 | 50.87 |
| | 50 | 0.990 | -1215 | 46.25 |
| | 60 | 0.848 | -1399 | 49.82 |

## CONCLUSSIONS

Pillared layer double hydroxides with $K_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$ was successfully conducted, which was identified from XRD analysis. XRD patterns showed optimal pillarizationresults at 12 hours by indicating the presence of double layer hydroxy material at $6^0$, $10^0$, and $35^0$ diffraction angles and in regions $60 - 63^0$ indicated the existence of pillarization process. The optimum adsorption of procion red was occurred at 20 minutes with adsorption of 57.45 ppm from initial concentration of 100 ppm. Procion red adsorption using pillarized compound resulted in adsorption rate (k) of 0.523 min$^{-1}$, while the influence of temperature and concentration of adsorption capacity is greatest at temperature 70 ºC. The largest adsorption energy at 70ºC is 125 kJ/mol, and for entropy ($\Delta S$) and enthalpy ($\Delta H$) decreases with increase of dye concentration.

## ACKNOWLEDGEMENT

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