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Research Paper

Modification Of Zn-Cr Layered Double Hydroxide With Keggin Ion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ as Cr(VI) Adsorbent

Melantina Oktriyanti[1], Neza Rahayu Palapa[1], Risfidian Mohadi [2], Aldes Lesbani [1,2]*

[1] *Graduate School of Chemistry, Faculty of Mathematic and Natural Sciences, Sriwijaya University, Jl. Padang Selasa Bukit Besar Palembang 30139, Indonesia*
[2] *Environmental Science Study, Graduate Program, Universitas Sriwijaya, Jl. Padang Selasa Bukit Besar Palembang 30139, Indonesia*
***Corresponding author e-mail**: aldeslesbani@pps.unsri.ac.id

Abstract
In this study, the synthesis of layered double hydroxide of Zn-Cr and Zn-Cr intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ have been conducted. The synthesized material was characterized using XRD, BET, and FTIR analyses. Zn-Cr layered double hydroxide and the intercalation were used as Cr(VI) ion adsorbent. Factors that influence the adsorption process, such as kinetic and thermodynamic parameters were studied. Based on XRD characterization, the interlayer distance Zn-Cr of layered double hydroxide was 7.53 Å increase to 10.26 Å on Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$. BET analysis showed that the surface area of both materials increased from 31.638 m2/g to 128.871 m2/g. The result of pH Point Zero Charge measurement for the Zn-Cr layered double hydroxide material was ten while the Zn-Cr intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ material was 8. Based on the kinetics model, adsorption of Cr(VI) ion follows pseudo-second-order model with a linear regression coefficient close to one. Furthermore, the Zn-Cr intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ shows the higher adsorption capacity for the Cr(VI) ion than the Zn-Cr layered double hydroxide as a control.

Keywords
adsorption, Cr(VI), Keggin ion, layered double hydroxide, Zn-Cr

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1. INTRODUCTION

Industrial activity is one of the most significant contributors of metal pollutants. Metal exposure from industrial waste is a serious concern because of the high level of poisoning and can accumulate in the ecosystem. One of the toxic heavy metal in the environment is chromium (VI) ion come from burning petroleum, chromium mining, and electroplating. The chromium ion maximum level in the environment according to the Indonesian government rule No.82/2001 is 0.05 mg/L. The efforts are needed to minimize Cr(VI) ions in the environment. Many methods have been developed to reduce metal pollutants from wastewater such as separating using membranes, ion exchange, and adsorption. One way of treating wastewater that is easy and environmentally friendly is adsorption. Adsorption has been chosen because it is more effective and easier to do (Nimibofa et al., 2015; Palapa et al., 2018). Adsorption methods that widely used include using materials from nature, such as activated carbon, zeolites, and silica gel. Activated carbon is known to adsorb heavy metals (Fu and Wang, 2011), while zeolites and silica gel can adsorb heavy metals and organic matter (Zhao et al., 2011). However, this material has several disadvantages, which are difficult to modify, and the structure tends to be stiff. In contrast to synthetic inorganic materials, the advantage of synthesized materials is that they are easier to modified as desired and are more flexibility properties. Its flexible nature makes such material layered double hydroxide interesting to study (Zhao et al., 2011; Nidheesh et al., 2018).

The benefits of layered double hydroxide are that it can be used as an adsorbent for dyes and heavy metals. For example, adsorbing a purplish red dye solution using Ni/Fe layered double hydroxide (Lei et al., 2017). The use of Ni/Fe and Mg/Fe layered double hydroxide for the adsorption of methyl orange dyes and methylene blue (Elmoubarki et al., 2017). According to Taher et al. (2019), heavy metals like iron(II) were removal using Ca/Al layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$. It's was effectively used than before intercalated. Lesbani et al. (2018) reported Cd (II) ion were removed by Zn/Al layered double hydroxide.

In this research, Zn-Cr layered double hydroxide was syn-

thesized by coprecipitation method and modification using an intercalation process with the Keggin ion $[SiW_{12}O_{40}]^{4-}$. The use of Keggin ions $[SiW_{12}O_{40}]^{4-}$ as an interconnect to produce higher interlayer distance. Modified material has been higher interlayer distance between layers, the value of adsorption capacity can be higher than without intercalation. The synthesized material was characterized using X-ray diffractometer, surface area analysis (BET), and infrared analysis (FTIR). Zn-Cr layered double hydroxide and intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ ions were applied as Cr(VI) ion adsorbent. Factors that influence the adsorption process were studied on the kinetic and thermodynamic parameters in the adsorption process such as adsorption time, the concentration of chromium ion and temperature effect.

2. EXPERIMENTAL SECTION

2.1 Material

The chemicals were supplied from Merck and Sigma-Aldrich such as zinc(II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot {}_6H_2O$), chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot {}_9H_2O$), sodium carbonate ($Na_2CO_3$), sodium hydroxide (NaOH), disodium tungstate dihydrate ($Na_2WO_4 \cdot {}_2H_2O$), sodium metasilicate (Na_2SiO_3), hydrogen chloride (HCl), potassium chloride (KCl), potassium dichromate ($K_2Cr_2O_7$), 1,5-diphenylcarbazide. XRD analysis was performed using the Rigaku Miniflex X-Ray diffractometer. BET surface area analysis was conducted Quantachrome adsorption-desorption apparatus. FTIR analysis was carried out using Shimadzu Prestige-21 at wavenumber 400-4000 cm^{-1} wavenumbers. Cr(VI) concentration analysis was performed using a UV-Vis Biobase spectrophotometer using 1.5-diphenylcarbazide as a complexing agent.

2.2 Method

2.2.1 Synthesis of Zn-Cr Layered Double Hydroxide

Zn-Cr layered double hydroxide was synthesized by coprecipitation method. A total of 13.07 g $Zn(NO_3)_2 \cdot {}_6H_2O$ was diluted in a 100 mL measuring flask. Then weighed $Cr(NO_3)_3 \cdot {}_9H_2O$ as much as 10.04 g and diluted in a 100 mL. $Zn(NO_3)_2 \cdot {}_6H_2O$ solution was mixed with a solution of $Cr(NO_3)_3 \cdot {}_9H_2O$, which was in 2:1 molarity ratio. The solution was dropped on a mixture of 2.5 M Na2CO3 and 3 M NaOH with a stir for 2 hours. The mixture solution was adjusted to pH 10 and was heated at 60 °C for 24 hours. The solution was filtered, washed with distilled water and the precipitate was dried at 60 °C (Hirata et al., 2015). Layered double hydroxide was characterized using XRD, BET, and FTIR analyses.

2.2.2 Synthesis of Polyoxometalate $K_4[\alpha-SiW_{12}O_{40}]$

Compound $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ was synthesized by dissolving 11 g of sodium metasilicate in 100 mL of water (solution A). Sodium tungstate 182 g was dissolved in 300 mL of hot water (solution B). The solution of HCl 4 M was added dropwise for 5 minutes into solution B with rapid stirring to dissolve the sediment from tungstic acid. Then, solution A was added quickly to solution B followed by the addition of 50 mL 4M HCl. The solution was maintained for 1 hour at 100 °C at a pH 5-6. A total of 50 mL of 1M sodium tungstate and 80 mL of 4M HCL was added to the solution quickly. This solution was filtered after being cooled at room temperature. The solution was used to obtain salt or $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ acids. Potassium salt was obtained by adjusting the solution to the pH 5 using KCl as much as 50 g quickly to get a white precipitate from potassium salt to form $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ (Ginsberg, 1990). Characterization of $K_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ was carried out using XRD and FTIR analyses.

2.2.3 Intercalation of Zn-Cr Layered Double Hydroxide with $[SiW_{12}O_{40}]^{4-}$

Intercalation of layered double hydroxide with polyoxometalate was conducted using ion exchange method. Polyoxometalate $K_4[\alpha-SiW_{12}O_{40}]$ (1 g) was added with 50 mL of distilled water. 2 g of layered double hydroxide was added with 25 mL of NaOH 1 M as solution B. Solution A and solution B were mixed quickly under nitrogen atmospheric condition gas for 24 hours. Then the suspension was cooled and washed with water and dried at room temperature (Sari et al., 2017). The characterization of layered double hydroxide intercalated material was carried out using XRD, BET, and FTIR analyses.

3. RESULTS AND DISCUSSION

3.1 Characterization

In Figure 1(a) Zn-Cr layered double hydroxide has a strong diffraction peak of the plane (003) at a value of 2θ which was 11.74° with an intensity of 781 and has a basal spacing of 7.53 Å. The diffraction peaks of Zn-Cr layered double hydroxide material appear typical regions at an angle of 2θ at 23.49°(006), 34.33°(009), and 60.41°(110). In Figure 1(c) the diffraction peak 2θ possessed the $[SiW_{12}O_{40}]^{4-}$ ion is at an angle of 8°, 10°, 28°, 32° and 34°. The successful synthesis of polyoxometalate compounds was shown by the presence of a typical peak at 8°-10° and an angle of 28°-32° (Delgado et al., 2004). Zn-Cr layered double hydroxide intercalated $[SiW_{12}O_{40}]^{4-}$ was synthesized into the neck flask under nitrogen gas. The use of this nitrogen gas is to prevent the occurrence of auto-oxidation by O_2, so that during the intercalation process anion $[SiW_{12}O_{40}]^{4-}$ can easily be entered between the layers and substituted of nitrate anions.

Figure 1(b) shows diffraction pattern of Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ has the highest diffraction peak in the region of 8.62°, 23.39°, 34.23°, dan 60.88°, respectively with basal spacing of 10.26Å, 3.80Å, 2.62Å, and 1.52Å. From this data, it can be seen that the intercalation of the Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ has an increase in

Table 1. The interlayer distance of layered double hydroxide before and after the intercalation

Material	Peak 2θ	d (Å)
Zn-Cr-[NO_3]	11.74°	7.53
Zn-Cr-[$SiW_{12}O_{40}$]$^{4-}$	8.62°	10.26

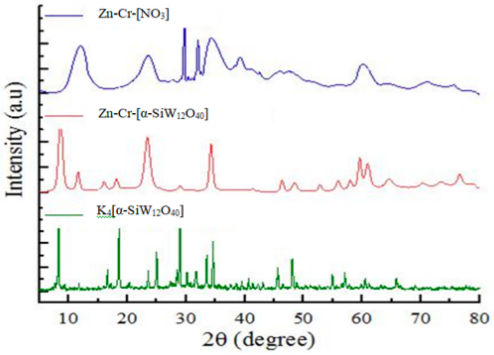

Figure 1. X-ray Diffactogram Pattern of Zn-Cr-[NO_3] (a), Zn-Cr-[$\alpha-SiW_{12}O_{40}$] (b), $K_4[\alpha-SiW_{12}O_{40}]$ (c)

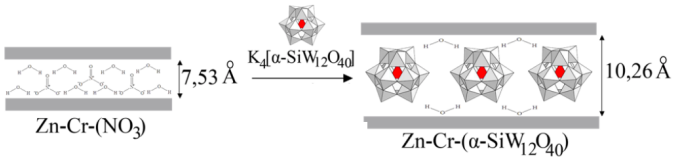

Figure 2. Illustration of Zn-Cr layered double hydroxide intercalated with Keggin ion [$\alpha-SiW_{12}O_{40}$]

the interlayer distance, which shows that the intercalation process has been successfully conducted. The interlayer distance of the layered double hydroxide material before and after the intercalation was shown in Table 1. Illustration of Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ shown as in Figure 2.

Desorption-adsorption isotherms of Zn-Cr layered double hydroxide and Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ are shown in Figure 3. In Figures 3 (a) and (b), a graph showing nitrogen adsorption-desorption isotherms on Zn-Cr layered double hydroxide and Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ belongs to type IV. Type IV isotherm curves belong to mesoporous material. The desorption curve follows a different path from the adsorption curve, causing hysteresis. The material in the form of mesoporous according to IUPAC is that which has a pore size of 2-50 nm. Zn-Cr layered double hydroxide isotherm graph and the results of its intercalation are in type H_2 adsorption-desorption isotherm. Material with type H_2 graph has a mesopore shape with wide loop pores (Alsamman, 2017).

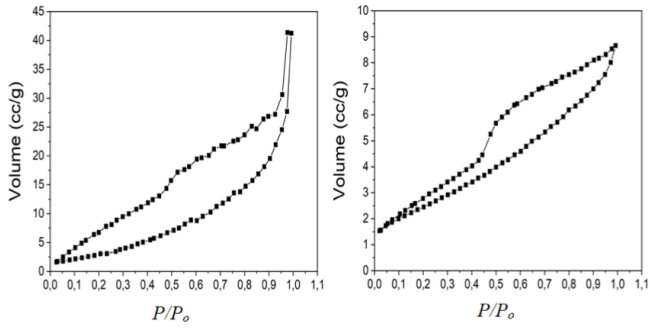

Figure 3. Nitrogen adsorption-desorption profile of (a) Zn-Cr layered double hydroxide and (b) Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$

The results of nitrogen adsorption-desorption isotherms analysis on Zn-Cr layered double hydroxide and the results of their intercalations produce data on surface area, volume, and pore diameter from the BET analysis as shown in Table 2. The data in Table 2 shows that there is an increase in the surface area of the Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$. In other hands, the pore volume of Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ had a larger pore volume compared to the pore volume of the Zn-Cr layered double hydroxide.

Characterization using FT-IR spectrophotometer was used to identify functional grup. Figure 4(a) shows that there is a bending and stretching vibration peak of the -OH group attached to the Zn-Cr layered double hydroxide at wavenumbers 1651.07 cm^{-1} and 3464.72 cm^{-1}. The emergence of the vibration peak in the area is known that there

Table 2. The results of the adsorption-desorption isotherm analysis

Material	Surface Area (m2/g)	Pore Volume(BJH) (cm3/g)	Pore Diameter (BJH) (nm)
Zn-Cr-[NO_3]	31.638	0.063	3.934
Zn-Cr-[$\alpha-SiW_{12}O_{40}$]	128.871	0.163	3.695

are anions in each of the layers of the material. The peak at wave number 1381.03 cm^{-1} indicates the NO_3^- anion stretching vibration, and the peak of Zn-O vibration and Cr-O vibration appear at wavenumbers 354.9 cm^{-1} and 848.68 cm^{-1}. On the other hand, figure 4(c) shows there is a vibration peak at wavenumber 3417.86 cm^{-1} in the $K_4[\alpha-SiW_{12}O_{40}]$ polyoxometalate compound. It is identifying the presence of H_2O contained in the $K_4[\alpha-SiW_{12}O_{40}]$. Polyoxometalate compound $K_4[\alpha-SiW_{12}O_{40}]$ has the characteristic shown in wave number 980 cm^{-1} which is the vibration of W=O. Wavenumber 902.69 cm-1 shows Si-O vibrations and wavenumber 794.67 cm^{-1} was assigned W-O-W vibrations.

Figure 4(b) shows the FT-IR spectra of the Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$. The vibration peaks was approved at the wavenumbers 354.9 cm^{-1} and 848.68 cm^{-1} which shows the vibrations of Zn-O and Cr-O (Hirata et al., 2015). At wave number 840.96 cm^{-1} shows the vibrations of Si-O. The vibration peak at the wavenumber of 516.92 cm-1 indicates the vibration of the W-Oc-W group. At a wavelength of 1381.03 cm^{-1}, there is a broad peak that shows a portion of the nitrate anion which has been substituted by $[SiW_{12}O_{40}]^{4-}$ anion from the $K_4[\alpha-SiW_{12}O_{40}]$ polyoxometalate.

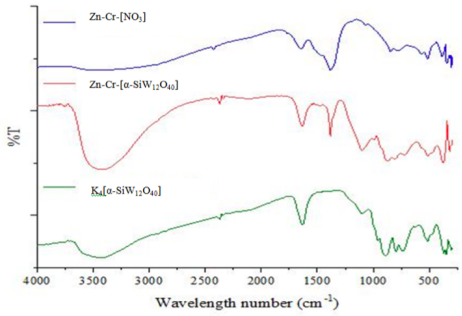

Figure 4. FTIR Spectra Zn-Cr-[NO_3] (a), Zn-Cr-[$\alpha-SiW_{12}O_{40}$] (b), $K_4[\alpha-SiW_{12}O_{40}]$ (c)

3.2 Determination of pH pzc

The plot results of determining pH pzc Zn-Cr layered double hydroxide and Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ are shown in Figure 5. In Figure 5, it can be seen that the Zn-Cr layered double hydroxide material has a intersection point at pH 10, which indicates no charge in the initial and final pH. Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ has a point intersection at pH 8. This occurs because of the interaction between positive ions and negative ions with NaCl. Zn-Cr layered double hydroxide and Zn-Cr layered double hydroxide intercalated are used as Cr (VI) ion adsorbents with the adsorption process carried out at pH pzc at pH 10 for Zn-Cr LDH and pH 8 for intercalated Zn-Cr.

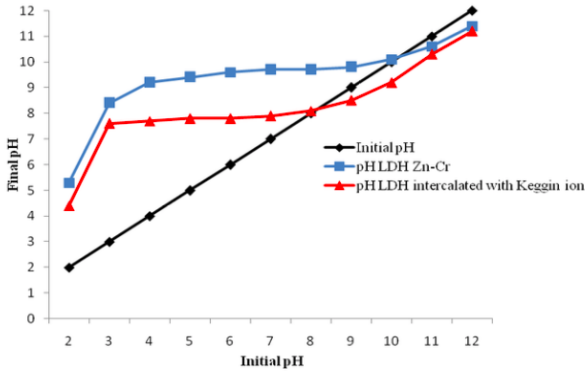

Figure 5. Graph of pH Point Zero Charge

3.3 Adsorption

3.3.1 Effect of Time of Cr(VI) Adsorption

The effect of adsorption time of Zn-Cr layered double hydroxide and Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ was studied by varying the contact time of adsorbant with an adsorbate. As much as 50 mg of layered double hydroxide sample or intercalated layered double hydroxide is added to a 100 mL erlenmeyer containing 50 mL of Cr(VI) solution with a concentration of 50 mg/L that has been adjusted to pH value according to pzc pH data, stirring using a magnetic stir bar with variations time 0, 5, 10, 15, 20, 50, 70, 90, 120, 150, and 180 minutes. The adsorption data of Cr(VI) ions to contact time variations are shown in Figure 7.

Adsorption kinetics was calculated using pseudo first order and pseudo second order equation as follows:

$$log(Qe - Qt) = logQe - \frac{k1}{2,303}t \quad (1)$$

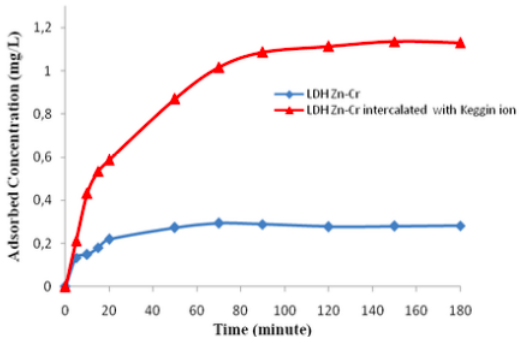

Figure 6. Effect of contact time of Cr(VI) ions with Zn-Cr layered double hydroxide adsorbents and intercalated Zn-Cr

$$\frac{t}{Qt} = \frac{1}{k2Qe^2} + \frac{1}{Qe}t \quad (2)$$

Qe = adsorption capacity at equilibrium (mg/g); Qt = adsorption capacity at t (mg/g); t = adsorption time (minute); k1 = kinetic adsorption rate at pseudo-first-order (minute^{-1}); k2 = kinetic adsorption rate at pseudo-second-order (g/mg minute)

Data from the variation of contact time of Cr(VI) ions with Zn-Cr layered double hydroxide and the results of their intercalations are used to determine the adsorption rate constant using the pseudo first order and the pseudo second order kinetic equation model. The data in Table 3 showed that adsorption of Cr(VI) follow kinetic pseudo second order for both layered double hydroxide. The Zn-Cr layered double hydroxide has a higher k_2 value, from 0.004 min^{-1} to 0.115 min^{-1}. It can be concluded that the layered double hydroxide is more reactive than the control layered double hydroxide.

3.3.2 Effect of Concentration and Temperature of Cr(VI) Adsorption

The influence of the adsorption temperature of Zn-Cr layered double hydroxide material and Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ were studied by varying the temperature during the adsorption process and the non-intercalated layered double hydroxide were used as controls. A total of 50 mg of layered double hydroxide or intercalated layered double hydroxide is added to a 100 mL erlenmeyer containing 50 mL of Cr(VI) solution with concentrations (5, 10, 15, 20 and 25) mg/L that have been adjusted to pH values according to pH pzc, stirring using a magnetic stir bar for 1.5 hours with variations in temperature (30, 40, 50, and 60) °C. The graph of effect of the concentration and temperature of Cr (VI) ion adsorption on Zn-Cr layered double hydroxide adsorbents and intercalated Zn-Cr layered double hydroxide is shown in Figure 7.

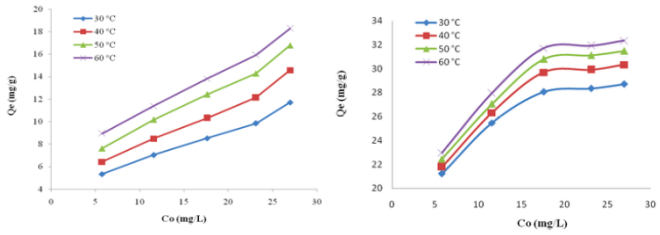

Figure 7. Effect of concentration and temperature of Cr(VI) with Zn-Cr layered double hydroxide adsorbent and Zn-Cr layered double hydroxide intercalated

The data in Figure 6 showed that the adsorption capacity of the Zn-Cr layered double hydroxide intercalated with Keggin ion $[SiW_{12}O_{40}]^{4-}$ is greater than the Zn-Cr layered double hydroxide. This is because the Zn-Cr layered double hydroxide intercalated has a large interlayer distance. This reason is equal with data of surface area, which intercalated material has higher surface area properties than material without intercalation.

Isotherm parameter was calculated based on the Langmuir and Freundlich equation as follows:

$$\frac{qe}{ce} = \frac{ce}{q_{max}} + \frac{1}{q_m K_L} \quad (3)$$

$$LogQe = logKF + \frac{1}{n} logCe \quad (4)$$

Ce = adsorbate concentration at equilibrium (mg/L); Qm = maximum adsorption capacity (mg/g); KL = Langmuir Isotherm constant; KF = Freundlich Isotherm constant; n = Freundlich Isotherm freedom degree

Data in figure 6 was used to obtain isotherm data as shown in Table 4. The approach of the adsorption isotherm model used is the Langmuir and Freundlich adsorption isotherm model. Isotherm Langmuir is meet for adsorption of Cr(VI) than Isotherm Freundlich for intercalated Zn-Cr. On the other hand Isotherm Freundlich is appropriate for Zn-Cr layered double hydroxide. This explains that the adsorption process is monolayer intercalated Zn-Cr and multilayer for Zn-Cr layered double hydroxide. Freundlich isotherm (n) freedom degree of more than 1 indicates that the adsorption process that occurs is multilayer physical adsorption. Thermodynamic data for adsorption of Cr(VI) on Zn-Cr and intercalated Zn-Cr layered double hydroxide is shown in Table 5 and 6.

From Table 5 and 6, it can be seen that the Cr(VI) ion adsorption process takes place spontaneously. A positive enthalpy value (ΔH) indicates that the adsorption process is endothermic. For the Gibbs free energy (ΔG), which is negative, which means the adsorption process is preferred at high temperatures. This is because the mobility of ions in the

Table 3. Kinetic adsorption model of Cr (VI) ions

Kinetic Models	Parameter	Zn-Cr-[NO3] LDH	Zn-Cr- [$SiW_{12}O_{40}$] LDH
Pseudo first order	Qe experiment (mg/g)	0.283	1.131
	Qe calculation (mg/g)	0.425	4.064
	k1 (g/mg min^{-1})	0.04	0.41
	R2	0.524	0.81
Pseudo second order	Qe experiment (mg/g)	0.283	1.131
	Qe calculation (mg/g)	0.293	1.253
	k2 (g/mg min^{-1})	0.004	0.115
	R2	0.996	0.989

Table 4. Adsorption isotherm model for adsorption of Cr(VI) on Zn-Cr and intercalated layered double hydroxide

Material	Temp (°C)	Adsorption Isotherm Models					
		Langmuir			Freundlich		
		Qm	KL	R2	n	KF	R2
Zn-Cr-NO3	30	15.873	0.088	0.926	2.232	2.576	0.97
	40	20	0.084	0.907	2.183	3.105	0.962
	50	22.222	0.1	0.939	2.288	3.926	0.976
	60	23.256	0.121	0.947	2.577	5.035	0.968
Zn-Cr-$SiW_{12}O_{40}$	30	30.303	1.269	0.999	8.475	20.324	0.982
	40	32.258	1.148	0.999	7.874	20.941	0.978
	50	33.333	1.2	0.998	7.937	21.777	0.978
	60	34.483	1.261	0.999	8.065	22.594	0.978

solution is higher because of the increase in temperature and the affinity of the adsorbate on the surface of the adsorbent is also higher. The entropy values (ΔS) in Table 5 and 6 show that the adsorption process is taking place on a regular basis. The smaller the value of entropy can create move organize the system.

4. CONCLUSIONS

Zn-Cr layered double hydroxide has been successfully intercalated using Keggin ion $[SiW_{12}O_{40}]^{4-}$. The XRD analysis results showed an increase in the distance from 7.53 Å to 10.26 Å. Furthermore, the BET analysis results showed an increase in the surface area of the Zn-Cr layered double hydroxide intercalated up to 128.871 m^2/g. The results of thermodynamic parameters show the physical adsorption process in this research which is endothermic and spontaneous. The result of Cr(VI) adsorption on the Zn-Cr layered double hydroxide intercalated has a higher adsorption reactivity indicated by a higher adsorption capacity of Cr(VI) ions.

5. ACKNOWLEDGMENT

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Table 5. Data enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG) and adsorption capacity (Qe) of the adsorption of Cr(VI) on Zn-Cr-[NO3] layered double hydroxide

Concentration	T (K)	Qe (mg/g)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
25 mg/L	303	11.708	13.992	0.04	1.872
	313	14.564			1.472
	323	16.777			1.072
	333	18.277			0.672

Table 6. Data enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG) and adsorption capacity (Qe) of the adsorption of Cr(VI) on Zn-Cr-$SiW_{12}O_{40}$ layered double hydroxide

Concentration	T (K)	Qe (mg/g)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
25 mg/L	303	28.7	4.529	0.017	-0.622
	313	30.342			-0.792
	323	31.484			-0.962
	333	32.341			-1.132

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