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Effective Removal of Iron (II) from Aqueous Solution by Adsorption using Zn/Cr Layered Double Hydroxides Intercalated with Keggin Ion

Melantina Oktriyanti[1], Neza Rahayu Palapa[1], RisfidianMohadi[1], Aldes Lesbani[1*]

[1] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sriwijaya University, Jl. Padang Selasa Bukit Besar Palembang 30139, Indonesia.

* Corresponding author's e-mail: aldeslesbani@pps.unsri.ac.id

ABSTRACT

Zn/Cr and Zn/Cr layered double hydroxides (LDHs) intercalated with Keggin ion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ were successfully synthesized at room temperature and pH value of 10. The synthesized materials were characterized by means of the XRD, BET, and FT-IR analyses and used as an adsorbent iron(II). The adsorption process was investigated by studying pH, the kinetics, and thermodynamic properties of the adsorption process. The results showed the interlayer Zn/Cr LDHs was 7.53 Å and increase to 10.26 Å on Zn/Cr LDHs intercalated with Keggin ion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$. The BET analysis showed that the pore volume of both materials increased from 0.063 $cm^3\ g^{-1}$ to 0.163 $cm^3\ g^{-1}$. The pH point zero charge measurement for the Zn/Cr LDHs material was 10 while LDHs Zn/Cr intercalated with Keggin ion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ was 8. Zn/Cr LDHs intercalated with Keggin ion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ has higher adsorption capacity than Zn/Cr LDHs without intercalation. Desorption of iron (III) was successfully conducted using HCl as reagent showing the involvement of ion exchange in the adsorption.

Keywords: Adsorption, Iron(II), Desorption, Zn/Cr, Layered double hydroxides.

INTRODUCTION

The heavy metal exposure that resulted from the industrial activities is now becoming a serious concern for researchers [Cherfi et al. 2014]. One of the heavy metals that have high toxicity because its risk for digestion when accumulates in the body is iron (II) [Fu et al. 2014]. Moreover, according to Indonesian Government regulation No.82/2001, the maximum iron (II) levels for drinking water and raw water fishery activities are 5 mg L^{-1}. There are several ways to reduce the heavy metal waste, such as ion exchange [Fu and Wang 2011], membrane [Lü et al. 2019], filtration and also adsorption [Huang et al. 2019; Peligro et al. 2016]. Among these methods, the adsorption is a suitable process due to the simple operation low cost and fast process [Oktriyanti et al. 2019]. Various adsorbents have been used as metal ion adsorption, such as cellulose [Wang et al. 2017], chitin [Boulaiche, Hamdi, and Trari 2019], chitosan [Zubieta et al. 2008], zeolite [Abdelrahman 2018], bentonite [Taher et al. 2017] and layered double hydroxides. [Wang et al. 2017] used the cellulose modified from sugar cane to remove Zn^{2+} with the maximum uptake of 363 mg/g. On the other hand, the adsorption of Cd^{2+} from aqueous solution using chitin has maximum uptake of 100 mg/g [Boulaiche et al. 2019]. The adsorption of Cu^{2+} using zeolite was reported by [Oliveira et al. 2019] with maximum uptake 142 mg/g. [Taher et al. 2019] reported that Ca/Al layered double hydroxides adsorbed iron (III) in aqueous solution with maximum uptake 11 mg/g. The studies on the application of layered double hydroxide as an adsorbent of heavy metals have been conducted successfully. As the study conducted by [Lesbani et al. 2018], the metal adsorption of Cd (II) can be conducted with the intercalated Zn/Al layered double hydroxide as an adsorbent. The research by [Zhou et al. 2018] reported the application of the Fe-Mn-Mg layer double hydroxide as

an adsorbent to remove Pb(II). [Tran et al. 2018] The removal of Cu(II) was effectively conducted using the Mg-Al layer double hydroxide as an adsorbent. Furthermore, the intercalated Mg-Al layer double hydroxide showed the adsorption properties for the removal of heavy metal from wastewater [Rahman et al. 2018]

In this research, Zn/Cr LDHs was synthesized through the co-precipitation method, then modified by the intercalation process using Keggin ions $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$. The Keggin $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ion was used as an intercalant species that aimed to produce a greater distance between layers, so it was expected that the adsorption process could be far more effective. Furthermore, the synthesized material was characterized using XRD, surface area analysis, and FTIR spectrophotometric analyses. The Zn/Cr layered double hydroxide intercalated Keggin ions $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ were further used as an adsorbent for the iron (II) removal by means of adsorption. The factors that influence the adsorption process were studied on the kinetic and thermodynamic parameters in the adsorption process.

MATERIALS AND METHODS

Chemical and Instrumentation

The chemicals used in this work, including $Zn(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, Na_2CO_3, NaOH, $Na_2WO_4 \cdot 2H_2O$, Na_2SiO_3, HCl, KCl, $FeCl_2 \cdot 4H_2O$, 1,10-phenanthroline monohydrate, acetate buffer, and hydroxylamine were obtained from Sigma Aldrich and Merck Chemicals and used as received without further purification. The XRD analysis was performed using the Rigaku Miniflex-6000 diffractometer and the sample was scanned at 10/deg. The BET surface area analysis was conducted using Quantachrome adsorption-desorption apparatus. The FT-IR analysis was identified using Shimadzu Prestige-21 by KBR pellet and the sample was analyzed at 400–4000 cm^{-1} wavenumbers.

Synthesis Zn/Cr LDHs

Zn/Cr LDHs were synthesized based on [Hirata, Tadanaga, and Tatsumisago 2015; Palapa et al. 2019] with a slight modification: $Zn(NO_3)_2.6H_2O$ (13.07 g) and $Cr(NO_3)_3 \cdot 9H_2O$ (10.04 g) were diluted in a 100 mL beaker flask with a molarity ratio of 2:1. The solution was mixed and poured into a mixture of 2.5 M Na_2CO_3 and 3 M NaOH then stirred for 2 hours. The pH value of 10 was adjusted by adding NaOH and then heating at 60°C for 24 hours to form Zn/Cr LDHs.

Intercalation of Zn/Cr LDHs with Keggin ions

Polyoxometalate compound of $K_4[\alpha\text{-}SiW_{12}O_{40}]$ nH_2O was synthesized according to the previously reported literature [Aparicio-Anglès et al. 2012]. The intercalation of layered double hydroxide by polyoxometalate was carried out as follows: 1 g of $K_4[\alpha\text{-}SiW_{12}O_{40}]$ polyoxometalate compound was added to 50 mL of distilled water whereas 2 g of layered double hydroxide was added to 25 mL of 1 M NaOH. Both solutions were mixed quickly under the N_2 gas conditions for 24 hours. The material was characterized using XRD, FTIR and BET analyses.

RESULTS AND DISCUSSION

Characterization of adsorbent

Characterization of the Zn/Cr and Zn/Cr LDHs material intercalated by Keggin ion was conducted using XRD, as shown in Figure 1. Figure 1(a) showed the strong diffraction peak of the Zn/Cr LDHs in plane (003) at an angle of 2θ is 11.74° with an intensity of 781 and basal spacing of 7.53 Å. The diffraction peaks that are typical of Zn/Cr LDHs material appear at an angle of 2θ at 23.49°(006), 34.33°(009), and 60.41°(110).

Figure 1(b) showed the highest diffraction peak in the Zn/Cr LDHs material intercalated by Keggin ions, which is in the 2θ value of 8.62° with a basal spacing of 10.26 Å, a peak at 23.39° with a basal spacing of 3.80 Å, a peak of 34.23°, and 60.88° having a basal spacing of 2.62 Å, and 1.52 Å, respectively. On the basis of on the data above, it can be seen that the intercalated Zn/Cr LDHs exhibited an increase in the distance higher than the original Zn/Cr LDHs, which shows the success of the material synthesis process. The success of the intercalation process was marked by the increase in the distance between layers of the LDHs material before and after the intercalation, as presented in Table 1.

The adsorption-desorption isotherms of Zn/Cr LDH and the intercalated Zn/Cr LDH are shown in Figure 2.

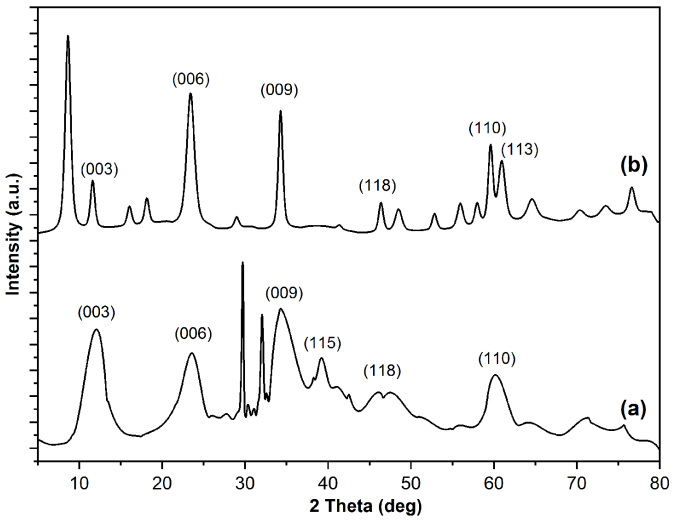

Figure 1. XRD powder patterns of Zn/Cr LDH (a) and Zn/Cr-[α-$SiW_{12}O_{40}$] (b)

Figure 2(a) and (b) show the graphs of nitrogen adsorption-desorption isotherms on Zn/Cr LDHs and intercalated Zn/Cr LDHs that indicated both materials followed type IV of isotherm pattern according to the IUPAC classification. Type IV isotherm curves belong to the mesoporous material because the desorption curve follows a different path from the adsorption curve, causing a hysteresis. The mesoporous material, according to IUPAC, has a pore size of 2–50 nm. The isotherm pattern of both Zn/Cr LDHs and intercalated Zn/Cr LDHs were included in type H2 because the material has wide and mesoporous shaped pores [Oktriyanti et al. 2019].

The results of the analysis of nitrogen adsorption-desorption isotherm on the Zn/Cr LDH and the intercalated Zn/Cr LDHs, including surface area, volume, and the pore diameter data from the BET analysis are shown in Table 2.

In Table 2, an increase in the pore volume of the material can be observed after intercalation. Intercalated Zn/Cr LDHs has a higher pore volume compared to the pore volume of Zn/Cr LDHs. The same phenomena happened to the surface area of the intercalated Zn/Cr LDHs, where it has a greater surface area than Zn/Cr LDHs. Zn/Cr and Zn/Cr LDHs intercalated by Keggin ion were identified using IR spectrophotometer and the results are shown in Figure 3.

Table 1. The value of the distance between the layered double hydroxide layer before and after intercalation

Materials	Angle 2θ	d (Å)	Distance Increased (Å)
Zn/Cr-[α-$SiW_{12}O_{40}$]	8.62°	10.26Å	2.73 Å
Zn/Cr	11.74°	7.53Å	

Figure 3(a) showed the bending vibrations and stretching peaks of the -OH group bound to the Zn/Cr layered double hydroxides, which was recorded at wavelengths of 1643.35 cm^{-1} and 3456.44 cm^{-1}. The vibration peaks that appeared in that area are marked by the presence of anions that occupied the layers space of material. The NO^{3-} anion stretching vibration was shown at a wavelength of 1381.03 cm^{-1}, and at a wavenumber of 339.47 cm^{-1} indicating that a peak of Zn-O vibrations (υ Zn-O), and Cr-O vibrations (υ Cr-O) appeared at a wavelength of 840.96 cm^{-1}. Figure 3(b) shows the FT-IR spectrum of the intercalated Zn/Cr LDH. In the FT-IR spectrum, the vibration peaks that can be observed at wavelengths of 354.9 cm^{-1} for Zn-O and 848.68 cm^{-1} were showed by the Cr-O vibrations [Hirata et al. 2015]. The vibrational peak of the (υ W-Oc-W) was at a wavelength of 509.21 cm^{-1} and the vibration of Si-O was shown at a wavelength of 871.82 cm^{-1}. The existence of a widening peak at a wavelength of 1381.03 cm^{-1} indicated a partial nitrate anion which has been substituted by a polyoxometalate compound.

Effect of initial pH

The adsorption process with the influence of pH was carried out by contacting 10 mL iron (II) (25 mg L^{-1}) with different pH 4,5,6,7,8,9,10, and 11 with 50 mg of Zn/Cr and Zn/Cr LDHs

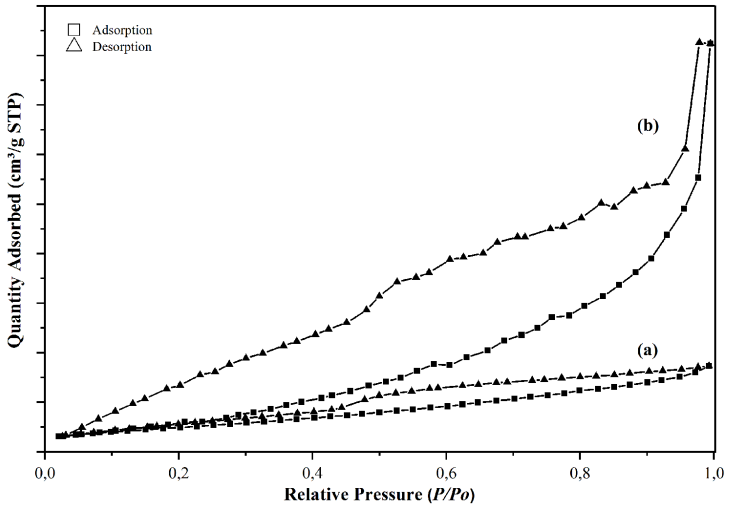

Figure 2. Profile of nitrogen adsorption-desorption of Zn/Cr LDHs intercalated by Keggin $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (a) and Zn/Cr LDHs (b)

Table 2. N2 adsorption-desorption properties of Zn/Cr and intercalated Zn/Cr LDHs

Kinetics model	Parameter	Zn/Cr LDH	Intercalated Zn/Cr LDH
Pseudo first order	Qe experiment (mg g^{-1})	4.359	8.900
	Qe calculated (mg g^{-1})	5.012	7.638
	k_1 (g mg^{-1} min^{-1})	0.035	0.055
	R^2	0.928	0.970
Pseudo second order	Qe experiment (mg g^{-1})	4.359	8.900
	Qecalculated (mg g^{-1})	4.975	9.346
	k_2 (g mg^{-1} min^{-1})	5.400	137.118
	R^2	0.980	0.998

intercalated with Keggin ion. The pH of the solution was studied to determine the optimum pH of iron (II) adsorption on the Zn/Cr and intercalated Zn/Cr LDHs. The influence of pH on the ability of the Zn/Cr layered double hydroxide and intercalated Zn/Cr layered double hydroxide can be seen in Figure 4.

The ability of Zn/Cr LDH for adsorbing iron (II) increases along with the pH condition until it reaches the optimum at pH 10 with an adsorption

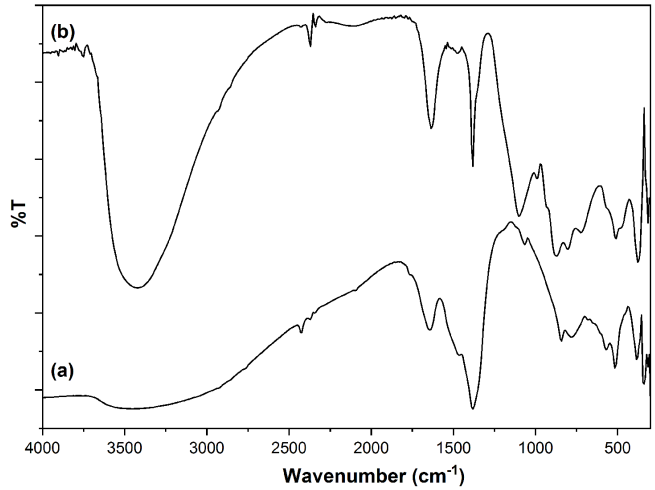

Figure 3. FT-IR spectra of Zn/Cr LDHs (a) and intercalated Zn/Cr LDHs (b)

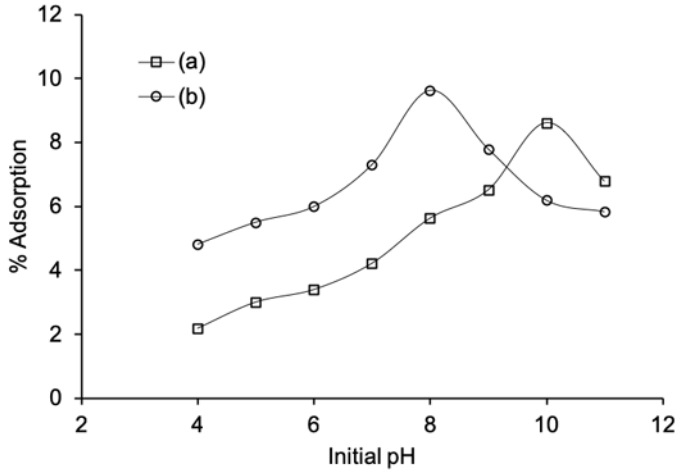

Figure 4. Effect of initial pH to the iron (II) uptake of Zn/Cr LDH (a) and intercalated Zn/Cr LDH (b)

capacity of 43.033 mg g^{-1}. The optimum pH for the intercalated Zn/Cr LDHs was observed at the value of 8 with an adsorption capacity of 48.115 mg g^{-1}. On the basis of these data, it can be observed that the higher the pH or the smaller the degree of acidity, the higher the adsorption power. This can happen because the pH of Zn/Cr LDH adsorbent was synthesized at basic pH so that under these conditions, the adsorbent can absorb the adsorbate more optimally.

Metal ion competition

The absorption ability of an adsorbent is highly influenced by the concentration of metal ions. The presence of the Cr(VI), Fe(II) and Cd(II) metal ions influences each other because it can reduce the efficiency and adsorption capacity. This phenomenon was affected by the competition between the metal ions over the active site of the adsorbent to form the adsorbate-adsorbent complex.

A total of 25 mL of each solution with a concentration of 25 mg L^{-1} was used to obtain a metal mixture, then 50 mL of the mixture was taken and added to 50 mg of Zn/Cr and intercalated Zn/Cr LDHs; then stirred for 2 hours and absorbance was measured afterwards. Table 3 Shows the competition of metal ions Cr(VI), Fe(II), and Cd(II) on the efficiency of Zn/Cr LDH and intercalated Zn/Cr LDH.

Table 3. Competition of Cr(VI), Fe(II), and Cd(II) metal ion against the adsorption efficiency of Zn/Cr LDH and intercalated Zn/Cr LDH

Materials	Surface area (m^2 g^{-1})	Pore Volume $_{BJH}$ (cm^3 g^{-1})	Pore Diameter $_{BJH}$ (nm)
Zn/Cr-[α-$SiW_{12}O_{40}$]	128.871	0.163	3.695
Zn/Cr	31.638	0.063	3.934

The value of Fe(II) metal adsorption efficiency was higher than Cr(VI) and Cd(II), which absorbed 19.426 mg L^{-1} for Zn/Cr LDHs and 20.590 mg L^{-1} for intercalated Zn/Cr LDHs. The amount of Fe(II) adsorption showed that the Zn/Cr and intercalated Zn/Cr LDHs can adsorb the Fe(II) metal ion in greater amount than Cr (VI) and Cd (II)

Effect of contact time

The effect of adsorption time on the adsorption of iron (II) into Zn/Cr and intercalated Zn/Cr LDHs was studied through the variations of the adsorbate contact time with the adsorbent. In the investigation, 50 mg of intercalated Zn/Cr or Zn/Cr LDHs was added into 50 mL of iron (II) solution with a concentration of 0.5 mg L^{-1} that had been adjusted to the pH values according to the pzc pH data. The mixture was stirred using a stirring bar magnet with time variations of 0, 5, 10, 15, 20, 50, 70, 90, 120, 150, and 180 minutes. The iron (II) adsorption data for variations in contact time are shown in Figure 5.

The adsorption kinetics was then determined based on the pseudo-first-order and pseudo-second-order model as described in the following equation.

$$\log (Q_e - Q_t) = \log Q_e \, (k_1/2.303) \quad (1)$$

$$t/Q_t = (1/k_2 Q_e^2) + (1/Q_e)\, t \quad (2)$$

where: Qe = adsorption capacity at equilibrium (mg g^{-1});

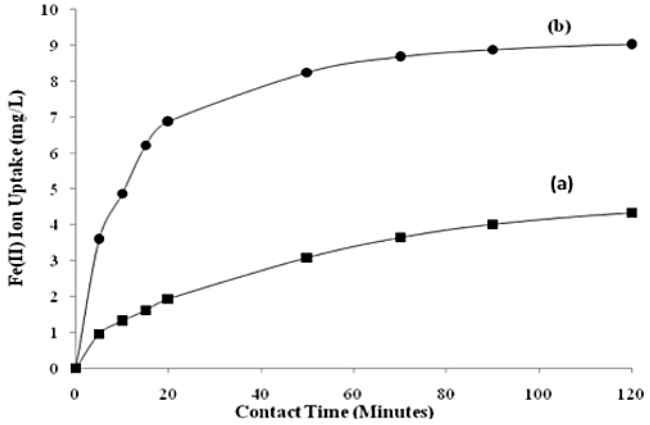

Figure 5. Effect of contact time versus the adsorption capacity of iron (II) onto Zn/Cr and intercalated Zn/Cr LDHs

Qt = adsorption capacity at t (mg g^{-1});
t = adsorption time (minute);
k_1 = kinetic adsorption rate at pseudo-first-order (min^{-1});
k_2 = kinetic adsorption rate at pseudo-second-order (g mg^{-1} min^{-1}).

The obtained data on the variation of contact time of iron (II) with Zn/Cr LDH and intercalated Zn/Cr LDH were used to determine the adsorption rate constant using the pseudo-first-order kinetic equation model and pseudo-second-order. The data in Table 4 shows the adsorption of iron (II) followed the equation of the pseudo-second-order kinetics model. It is indicated by the linear regression coefficient value of the intercalated Zn/Cr LDH reaching 0.998.

Effect of concentration and temperature adsorption

The effect of adsorption temperature on the adsorption capacity of Zn/Cr and intercalated Zn/Cr LDHs was studied by varying the temperature during the adsorption process. As much as 50 mg of intercalated Zn/Cr and Zn/Cr LDHs was added into 50 mL of iron (II) solution with the concentrations of 10, 15, 20, 25 and 30 mg L^{-1} that have been adjusted to the pH values according to pH pzc, then stirring using a magnetic stir bar for 2 hours with variations at a temperature of 30, 40, 50, and 60°C. The effect of the iron (II) concentration and adsorption temperature on the adsorption capacity of iron (II) on Zn/Cr and intercalated Zn/Cr LDHs can be seen in Figure 6.

Table 4. Adsorption kinetic model of iron(II) adsorption

Adsorbent	Metal Ion Adsorption (mg L^{-1})		
	Cr	Fe	Cd
Zn-Cr	0.097	19.426	3.449
Zn-Cr-[α-$SiW_{12}O_{40}$]	0.527	20.590	4.170

The obtained data indicated that the intercalated Zn/Cr LDHs have the largest adsorption capacity. These results can be achieved because the intercalated Zn/Cr LDHs have a greater basal spacing which causes greater absorption of iron (II) adsorbate. The isotherm parameters were calculated based on the Langmuir and Freundlich equations, as follows:

$$C_e/Q_e = (C_e/Q_m) + (1/Q_m k_L) \quad (3)$$

$$\text{Log } Q_e = \log k_F + 1/n \log C_e \quad (4)$$

where: Ce = adsorbate concentration at equilibrium (mg L^{-1});
Q_m = maximum adsorption capacity (mg g^{-1});
k_L = Langmuir isotherm constant;
k_F = Freundlich isotherm constant;
n = degree of isotherm freedom.

The adsorption isotherm models employed in this work were Langmuir and Freundlich. The adsorption isotherm model approach was also used to determine the adsorption thermodynamic parameter such as the changes of enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG).

The obtained results tabulated in Table 5 were calculated based on the Langmuir adsorption isotherm model. According to the obtained value, it can be described that the adsorption process was conducted in a physical way and in a monolayer system. The thermodynamic data

for the adsorption of iron (II) onto Zn/Cr LDH and intercalated Zn/Cr LDH can be shown in Tables 6 and 7.

According to Tables 5 and 6, it can be seen that the adsorption of iron (II) into both Zn/Cr LDH and intercalated Zn/Cr LDH occurred spontaneously. Moreover, from the obtained value of (ΔH), it can be described that the adsorption process did not need a huge amount of energy and it can be assumed that the interaction involved between the adsorbent and adsorbate was Van der Waals interaction. It also can be observed that the adsorption process occurred orderly.

Desorption study

Desorption is a phenomenon in which a substance escapes from the surface or removal of atoms, molecules or ions that are entangled on the surface. Desorption occurs when the adsorption process is maximized because the surface of the adsorbent is saturated or no longer able to absorb the adsorbate. In this work, the desorption study was carried out using certain solvents to test the extent to which a material can be reused.

The iron (II) desorption study was conducted on Zn/Cr and intercalated Zn/Cr LDHs. The solvents used in the desorption process were HCl, hot water, NaOH, $HONH_3Cl$, NaCl, H_2O, Na-EDTA, and diethyl ether. A total of 0.01 g of the used adsorbent was mixed into 10 mL of the solvent and then stirred reducing a magnetic stir bar at equilibrium for 2 hours. The data on the percent desorption of Zn/Cr LDH and intercalated Zn/Cr LDH can be seen in Figure 7.

The largest percentage of iron (II) desorption was obtained in the HCl solvent and in the Zn/Cr LDH adsorbent, reaching up to 93.24%. It can be assumed that in the acidic solvents, the iron (II) metal was ionized, so the ions that were trapped inside the surface of the material were desorbed more easily. Thus, the ion exchange mechanism on the adsorption of iron (II) was dominant in this research.

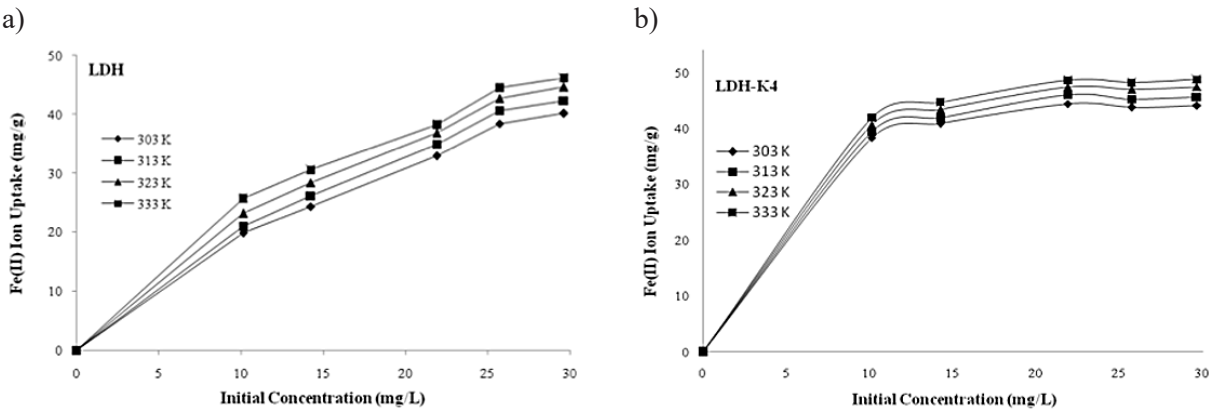

Figure 6. Effect of concentration and temperature on the adsorption of iron (II) onto Zn/Cr and intercalated Zn/Cr LDHs

Table 5. The adsorption isotherm data according to the Freundlich and Langmuir adsorption isotherm model

Material	Temperature (*K*)	Adsorption isotherm model					
		Langmuir			Freundlich		
		Q_m (mg g^{-1})	k_L (mg g^{-1})	R^2	n	k_F (mg g^{-1})	R^2
Zn/Cr LDH	303	76.923	0.054	0.965	1.704	6,699	0.990
	313	76.923	0.062	0.976	1.754	7.551	0.992
	323	71.429	0.082	0.979	1.961	9.572	0.992
	333	66.667	0.115	0.976	2,326	12.618	0.984
Intercalated Zn/Cr LDH	303	45.455	2.000	0.999	14.085	35.975	0.943
	313	47.619	2.100	0.999	14.085	37.239	0.938
	323	50.000	2.222	0.999	14.085	38.637	0.962
	333	50.000	2.500	0.999	15.385	40.365	0.966

Table 6. Adsorption thermodynamic properties of iron (II) onto Zn/Cr LDH

Concentration	T (K)	Q_e (mg g^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})	ΔG (kJ mol^{-1})
30 mg L^{-1}	303	40.109	5.604	0.024	-1.668
	313	42.240			-1.908
	323	44.590			-2.148
	333	46.120			-2.388

Table 7. Adsorption thermodynamic properties of iron(II) onto intercalated Zn/Cr LDH

Concentration	T (K)	Q_e (mg g^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})	ΔG (kJ mol^{-1})
30 mg L^{-1}	303	44.104	4.140	0.020	-1.920
	313	45.628			-2.120
	323	47.432			-2.320
	333	48.743			-2.520

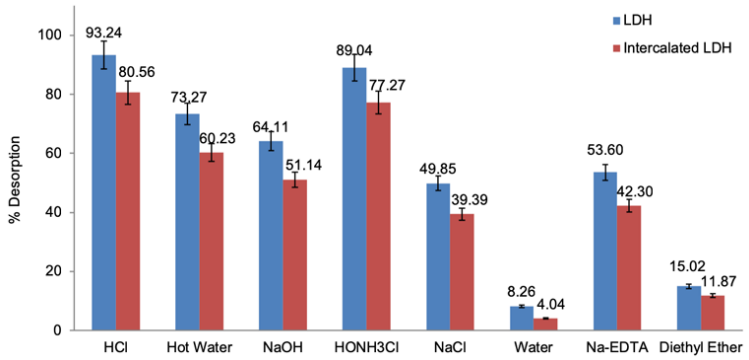

Figure 7. Desorption of iron (II) from the used Zn/Cr and intercalated Zn/Cr LDHs at different solvent

CONCLUSIONS

The Zn/Cr LDH was successfully intercalated using the Keggin $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ion. An increase in the distance between layers was observed from the XRD analysis results up to 10.26 Å. Furthermore, the results of BET analyses showed the surface area and pore volume was increased after intercalation. On the basis of the calculation, the thermodynamic parameters indicated that the adsorption process was physical and spontaneous. The intercalated Zn/Cr LDHs exhibited a greater adsorption capacity to iron (II) than Zn/Cr LDHs without intercalation. Moreover, the Zn/Cr and intercalated Zn/Cr LDHs adsorbent can be reused for a further adsorption process. This result based on the desorption cause that the iron(II) can be desorbed from the adsorbent in as much as 93.24%.

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REFERENCES

1. Abdelrahman, E.A. 2018. Synthesis of zeolite nanostructures from waste aluminum cans for efficient removal of malachite green dye from aqueous media. Journal of Molecular Liquids 253, 72–82.
2. Aparicio-Anglès, X., Miró, P., Clotet, A., Bo, C., Poblet, J. M. 2012. Polyoxometalates adsorbed on metallic surfaces: immediate reduction of [SiW 12O 40] 4- on Ag(100). Chemical Science 3(6), 2020–27.
3. Boulaiche, W., Hamdi, B., Trari, M. 2019. Removal of heavy metals by chitin: equilibrium, kinetic and thermodynamic studies. Applied Water Science 9(2), 1–10.
4. Cherfi, A., Abdoun, S., Gaci, O. 2014. Food survey: levels and potential health risks of Chromium, Lead, Zinc and Copper content in fruits and vegetables consumed in Algeria. Food and Chemical Toxicology 70, 48–53.

5. Fu, F., Dionysiou, D.D., Liu, H. 2014. The use of zero-valent iron for groundwater remediation and wastewater treatment: A review. Journal of Hazardous Materials 267, 194–205.
6. Fu, F., Wang, Q. 2011. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management 92(3), 407–18.
7. Hirata, N., Tadanaga, K., Tatsumisago, M. 2015. Photocatalytic O_2 evolution from water over Zn-Cr layered double hydroxides intercalated with inorganic anion. Materials Research Bulletin 62, 1–4.
8. Huang, D., Liu, C., Zhang, C., Deng, R., Wang, R., Xue, W., Luo, H., Zeng, G., Zhang, Q., Guo, X. 2019. Cr(VI) removal from aqueous solution using biochar modified with Mg/Al-layered double hydroxide intercalated with ethylenediaminetetraacetic acid. Bioresource Technology 276, 127–32.
9. Lesbani, A., Hensen, H., Taher, T., Hidayati, N., Mohadi, R., Andreas, R. 2018. Intercalation of Zn/Al layered double hydroxides with keggin ion as adsorbent of Cadmium(II). AIP Conference Proceedings, 2026.
10. Lü, Z., Hu, F., Li, H., Zhang, X., Yu, S., Liu, M., & Gao, C. 2019. Composite nanofiltration membrane with asymmetric selective separation layer for enhanced separation efficiency to anionic dye aqueous solution. Journal of Hazardous Materials 19, 436–43.
11. Oktriyanti, M., Palapa, N.R., Mohadi, R., Lesbani, A. 2019. Modification of Zn-Cr layered double hydroxide with keggin ion. Indonesian Journal of Environmental Management and Sustainability 3(3), 93–99.
12. Oliveira, J.A., Cunha, F.A., Ruotolo, L.A.M. 2019. Synthesis of zeolite from sugarcane bagasse fly ash and its application as a low-cost adsorbent to remove heavy metals. Journal of Cleaner Production 229, 956–63.
13. Palapa, N.R., Saria, Y., Taher, T., Mohadi, R., Lesbani, A. 2019. Synthesis and characterization of Zn/Al, Zn/Fe, and Zn/Cr layered double hydroxides: Effect of M^{3+} ions toward layer formation. Science and Technology Indonesia 4(2), 36–39.
14. Peligro, F.R., Pavlovic, I., Rojas, R., Barriga, C. 2016. Removal of heavy metals from simulated wastewater by in situ formation of layered double hydroxides. Chemical Engineering Journal. 306, 1035–1040
15. Rahman, M.T., Kameda, T., Kumagai, S., Yoshioka, T. 2018. A novel method to delaminate nitrate-intercalated Mg–Al layered double hydroxides in water and application in heavy metals removal from waste water. Chemosphere 203, 281–90.
16. Taher, T., Christina, M.M., Said, M., Hidayati, N., Ferlinahayati, F., Lesbani, A. 2019. Removal of iron(II) using intercalated Ca/Al layered double hydroxides with $[\text{-SiW}_{12}\ O_{40}]^{4-}$. Bulletin of Chemical Reaction Engineering & Catalysis 14(2), 260–67.
17. Taher, T., Mohadi, R., Rohendi, D., Lesbani, A. 2017. Kinetic and Thermodynamic adsorption studies of congo red on bentonite. AIP Conference Proceedings, 1823.
18. Tran, H.N., Lin, C.C., Woo, S. H., Chao, H.P. 2018. Efficient removal of Copper and Lead by Mg/Al layered double hydroxides intercalated with organic acid anions: Adsorption kinetics, isotherms, and thermodynamics. Applied Clay Science 154, 17–27.
19. Wang, F., Pan, Y., Cai, P., Guo, T., Xiao, H. 2017. Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent. Bioresource Technology 241, 482–90.
20. Zhou, H., Jiang, Z., Wei, S. 2018. A New Hydrotalcite-Like Absorbent FeMnMg-LDH and its adsorption capacity for Pb_2^+ ions in water. Applied Clay Science 153, 29–37.
21. Zubieta, C., Sierra, M.B., Morini, M.A., Schulz, P. C., Albertengo, L., Rodŕguez, M.S. 2008. The adsorption of dyes used in the textile industry on mesoporous materials. Colloid and Polymer Science 286(4), 377–84.