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Research Paper

Adsorption of Cobalt (II) on Layered Double Hydroxides (Mg/Al and Ca/Al) In Aqueous Medium : Kinetic and Thermodynamic Aspect

Neza Rahayu Palapa[1], Tarmizi Taher[2], Muhammad Said[1], Risfidian Mohadi[1], Aldes Lesbani[1]*

[1]*Magister of Chemistry, Faculty of Mathematic and Natural Sciences, Sriwijaya University, Jl.. Padang Selasa Bukit Besar Palembang 30139*
[2]*2Department of Enviromental Science, Graduate School, Sriwijaya University, Jl. Padang Selasa No. 524 Ilir Barat 1, Palembang-South Sumatra, Indonesia*
***Corresponding author**: aldeslesbani@pps.unsri.ac.id*

Abstract
Layered double hydroxides Mg/Al and Ca/Al has been synthesized by co-precipitation method with molar ratio M^{2+}:M^{3+} (3:1) at pH 10. The synthesized materials were characterized by XRD and FTIR. The materials were used as adsorbent for the removal Cobalt (II) in aqueous solution. The adsorption experiments were studied through some variables adsorption such as variation of contact time, variation of temperature and variation of initial concentration. Kinetic parameters was obtained from variation of contact time. Data was analyzed by pseudo-first-order and pseudo-second-order kinetics models in linear analyses. The kinetic studies showed that the adsorption process more fitted by pseudo-second-order than pseudo-first-order based on coefficient correlation. Isotherm parameters was calculated using Langmuir and Freundlich isotherm models. The adsorption process was spontaneous and endothermic.

Keywords
layered double hydroxides, adsorption, Cobalt (II)

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1. INTRODUCTION

Layered material are classified into two groups, cationic clays and anionic clays. Cationic clays are found in nature and anionic clays are easily synthesized. Layered double hydroxides (LDH) belong to the anionic clay minerals was consist of sheets of the hydroxides of two metals different valence. The metals hydroxides layeres are positively charged, so neutrality charged requires must be anion intercalated into interlayer. Usually, hydroxil ions was present as anion and this anion can be readily exchanged by others such as carbonate ions (Rosenberg and Armstrong, 2016).

LDHs has general formula $[M^{2+}(1\text{-}x)M^{3+}x(OH)_2](An\text{-})x/nH_2O$, where M^{2+} and M^{3+} are di-valent and tri-valent cations such as Mg^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+} and Al^{3+}, Cr^{3+}, Ga^{3+}, Mn^{3+} or Fe^{3+} (Hongo et al., 2017). This layer materials have high flexibility cation exchange and easily synthesized in laboratory (Zhao et al., 2011). Layered double hydroxide has many potential aplications for layered double hydroxides including catalysis, adsorption and flame retardant composite (Clark et al., 2017).

There have been many studies were focusing on the aplication of layered double hydroxides as adsorbent Zhao et al. (2011); El-Sayed et al. (2016); Said and Palapa (2017). Layered double hydroxides was used to adsorpted heavy metals Zhao et al. (2011) and stable at pH >5 up to 12 (Costantino et al., 2013). As known, the presence of heavy metals in the environment can be harmful to variety of living species. Therefor, the removal of heavy metals from waste water is important to public health. The industrial waste water usually containing cobalt (II) is common. The adsorption of heavy metals in solution can be removed using several technique such as adsorption, precipitation, coagulation, chemical precipitation, ion-exchange, ozonation and membran filtration (Shou et al., 2015). The adsorption is recognized as an easy, economic and effective to removed heavy metals from the waste water (El-Sayed et al., 2016; Taher et al., 2018).

In this research, synthesis and characterization of layered double hydroxides was conducted using Frourier Transform Infra Red (FT-IR) and X-Ray Difractometer (XRD). The adsorption process of layered double hydroxides is intended to determine the kinetic and thermodynamic parameters by measuring residual concentration and adsorbed using Atomic Adsorption Spectrophotometer.

2. EXPERIMENTAL SECTION

The chemicals used are analytical grade such as magnesium nitrate, alumunium nitrate, calsium nitrate, sodium carbon-

ate, sodium hydroxide and cobalt nitrate. Water was supplied from Integrated Research Lab Graduated School, Sriwijaya University. Analysis instrument were used FT-IR Shimadzu Prestige-21, XRD Shimadzu Lab X-Type 6000 and Atomic Adsorption Spectrophotometer NovAA 350 Analytic Jena.

2.1 Synthesis of Layered Double Hydroxides

Synthesis of layered double hydroxides Mg/Al was conducted according to (Palapa and Said, 2016). Synthesis of layered double hydroxides Ca/Al was conducting using 100 mL of a solution containing 0.3 mol $Ca(NO_3)_2 \cdot H_2O$ and 0.1 mol $Al(NO_3) \cdot {}_9H_2O$ under vigorous stirring, while was added dropwise 2 mol/L of NaOH at pH 11 then stirring until 24 h to form white solid material and dried at room temperature to obtain Ca/Al layered double hydroxides (Rojas, 2014).

2.2 Adsorption Experiment

Kinetic Parameter 0.05 g layered double hydroxides Mg/Al and Ca/Al each added into 50 mL of cobalt (II) shaker with variations in contact time varied. The solution of the adsorbed cobalt (II) substance was separated by filtration and then measured its concentration by using Atomic Adsorption Spectrophotometer. **Thermodynamic Parameter** Thermodynamic adsorption of cobalt (II) using adsorbent 0.05 g layered double hydroxides Mg/Al and Ca/Al each added into 50 mL cobalt (II) by variying the with each adsorption temperature is 30 °C, 35 °C, 40 °C, 45 °C, 50 °C. The solution of the adsorbed cobalt (II) substance was separated by filtration and then measured its concentration by using Atomic Adsorption Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

Characterization of layered double hydroxide was carried out using the FT-IR. The FT-IR of the layered double hydroxides Mg/Al and Ca/Al is shown in Figure 1. The vibration at wavenumber 3300-3800 cm^{-1} is assigned as streching of O-H and the bending of O-H at 1635 cm^{-1}. The bending of nitrate is appeared at wavenumber 1381-1388 cm^{-1}. These vibration was unique vibration for layered double hydroxides. The vibrations of Al-O, Ca-O and Mg-O were appreated at 563 cm^{-1} , 424 cm^{-1} and 416 cm^{-1} respectively.

The XRD patterns of Mg/Al and Ca/Al material were shown in Figure 2. The unique structure of layered double hydroxides was identified at diffraction angle. This difraction 100 and 600 indicated that presence of layered materials and the anion on the interlayered. XRD pattern of Ca/Al in Figure2b was shown semiliar to that reported by Hongo et al. (2017) when synthesis of material was carried out at temperature was 27 °C (room temperature), the peak intensity of calcite was stong, its because layered double hydroxides contained calcite.

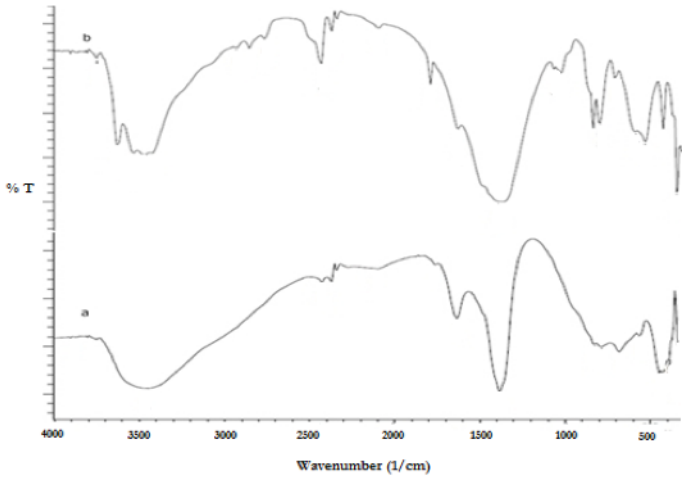

Figure 1. FT-IR spectrum of layered double hydroxides Mg/Al (a) and layered double hydroxides Ca/Al (b)

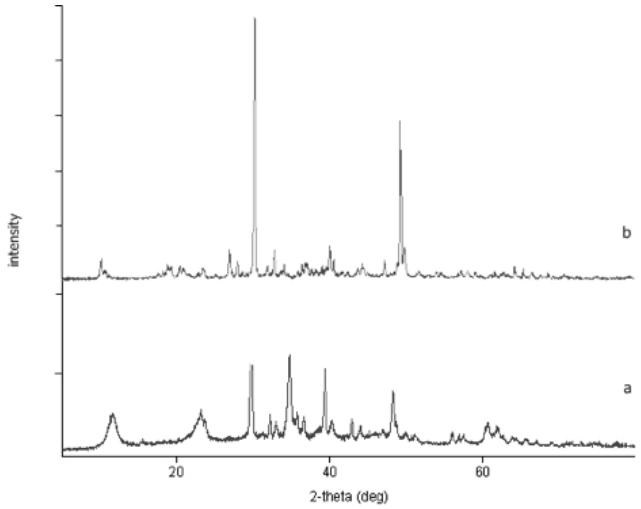

Figure 2. XRD patterns of layered double hydroxides Mg/Al (a) and layered double hydroxides Ca/Al (b)

3.2 Kinetic Adsorption of Cobalt (II) on Mg/Al and Ca/Al Layered Double Hydorxides

In order to establish the equilibrium time for maximum adsorption, the adsorption of of cobalt (II) was investigated as the function of contact time. Kinetic adsorption of cobalt (II) on layered double hydroxides Mg/Al and Ca/Al was studied by investigated adsorption time as shown in Figure 3.

Figure 3 shows that Mg/Al and C/Al layered double hydroxide increased slowly after an hour with percentage adsorp 84% and 78%, respectively. The fast removal adsorption can happen because the adsorbent surfaces have large number of site to adsorb Co(II) solution, then the rate of adsorbent was decreased when the surface site full of adsorbate accumulated. To identify the rate kinetics of the adsorption process, two kinetics models, namely the pseudo-first-order (PFO) and seudo-second-order (PSO) have been employed to fit the experimental data. The

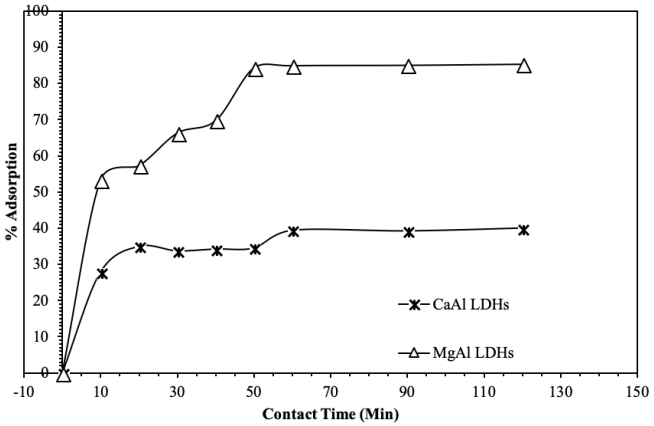

Figure 3. Effect of contact time on the adsorption of Cobalt (II) onto Mg/Al and Ca/Al LDHs

pseudo-first-order kinetics model desribes the adsorption of liquid/solid system based on solid capacity. The model can be written as:

$$\frac{dqt}{dt} = k1(qe - qt) \tag{1}$$

$$log(qe - qt) = logqe - \frac{k1}{2.303}t \tag{2}$$

where qe and qt are the capacity of metal ions adsorbed (mg g^{-1}) at equilibrium and time t (h), respectively, and K1 is the PFO rate constant(h^{-1}).

Thus the value of qe and k1 can be determined experimentally by plotting log(qe-qt) versus t and extracting information from the least squares analysis of slope and intersept into eq (1). The seudo-second-order adsorption kinetic is expressed as following formulation:

$$\frac{dqt}{dt} = k2(qe - qt)^2 \tag{3}$$

$$\frac{t}{qt} = \frac{1}{k2qe^2} + \frac{1}{qe}t \tag{4}$$

Where k2 (g mg^{-1} h^{-1}) is the PSO rate constant for the adsorption process. Thus values of k2 and qe can be calculated from intercept and the slope of the linear relationship eq (4) between t/qt and t.

The calculated values of k1 , k2 , and coefficient correlation (R^2) obtain in Table 1. The result indicated that linear of PFO model did not give reasonable values with regard to the experimentals of Co(II). However, the (R^2) values are low for linear PFO comparing with (R^2) values obtain from PSO. These result suggest that the second order mechanism is predominant, in which the adsorption mechanism depends on the adsorbate and adsorbent.

Table 1. Kinetics models for the adsorption of Co (II)

kinetics models	parameters	Adsorbent Mg/Al	Adsorbent Ca/Al
Pseudo-first-order	qe exp (mg/g)	17.0769	16.9949
	qe calc (mg/g)	18.7013	13.2092
	k1 (min-1)	0.0714	0.0359
	R^2	0.9367	0.9722
Pseudo-Seconds-order	qe exp (mg/g)	17.0769	16.9949
	qe calc (mg/g)	18.7798	18.3765
	k2 (min-1)	0.0053	0.0185
	R^2	0.992	0.995

The result was shown in Table 1. Table 1 was calculated value of k1 and k2, qe exp, qe calc together with (R^2). The value of correlation coefficient MgAl and Ca/Al (R^2) = 0.99 for pseudo-second-order model was better fitted than pseudo-first-orde for adsorption Co(II) by MgAl and Ca/Al layered double hydroxides, respectively. The data obtained in Table 1 also showed that the layered double hydroxides Mg/Al has a more reactive than Ca/Al because layered double hydroxides Mg/Al has the adsorption rate (0.0053 (min^{-1})) lower than layered double hydroxides Ca/Al (min^{-1}).

3.3 Thermodynamic Adsorption of Cobalt (II) on Mg/Al and Ca/Al Layered Double Hydroxides

The Thermodinamics parameters was studied by varied of concentration and temperature. Thermodynamics were used two models isotherm for this data Langmuir and Freundlich ishotherm models. The Langmuir assumed that adsorbate was occupied onto monolayer. Its used equation as follows:

$$\frac{Ce}{qe} = \frac{1}{kLqmax} + \frac{Ce}{qmax} \tag{5}$$

Where qe is the equilibrium adsorption, Ce is equilibrium concentration, qmax is the maximum adsorption and kL is the equilibrium adsorption constant. Then, the essential features of Langmuir isotherm namely RL (equilibrium parameters). Value RL has indicated the models of isotherm. If irreversible, the RL calculated zero (RL = 0), liniear when RL = 1, and favorable when 0> RL>1 (Kumar et al., 2012).

The Freundlich isotherm model identified the heterogenous adsorbent surface. The equation is following:

$$Logqe = LogkF + nLogCe \tag{6}$$

Where kF is adsorption capacity when equilibrium. Thermodynamic adsorption of cobalt (II) on layered double hydroxides Mg/Al and Ca/Al was studied by variying concentration and temperature. Adsorption data by layered double hydroxides Mg/Al and Ca/Al in Figure 4 and Figure 5. Therefore, both the isotherm models are shown in Table 2. Based on correlation

Table 2. Langmuir and Freundlich Isotherm Models

Correlation Parameter	T= 303 K		T= 308 K		T= 313 K		T= 318 K	
Langmuir	Mg/Al	Ca/Al	Mg/Al	Ca/Al	Mg/Al	Ca/Al	Mg/Al	Ca/Al
Qmax	18.288	17.453	22.726	18.463	25.773	21.098	36.855	21.318
KL	0.0626	0.071	0.085	0.077	0.080	0.070	0.0557	0.073
RL	0.00068-0.0054	0.00071-0.0056	0.00054-0.0043	0.00067-0.0054	0.00048-0.0035	0.00059-0.0047	0.00033-0.0027	0.00058-0.00046
R^2	0.996	0.994	0.995	0.994	0.995	0.992	0.994	0.991
Freundlich	Mg/Al	Ca/Al	Mg/Al	Ca/Al	Mg/Al	Ca/Al	Mg/Al	Ca/Al
Kf	1.391	1.933	2.025	2.040	1.969	1.847	2.1433	2.149
n	1.505	1.802	1.476	1.856	1.366	1.537	1.299	1.609
R^2	0.894	0.706	0.741	0.718	0.798	0.677	0.848	0.829

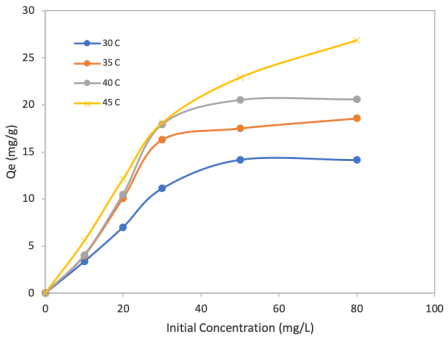

Figure 4. Adsorption of cobalt (II) varied concentration and temperature by layered double hydroxides Mg/Al

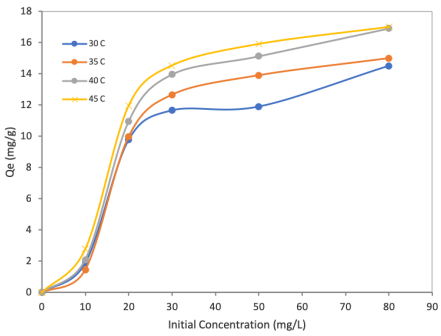

Figure 5. Adsorption of cobalt (II) varied concentration and temperature by layered double hydroxides Ca/Al

coefficient of the data, Langmuir isotherm models more fitted than Freundlich isotherm models. Its indicated the adsorption was accour in monolayer adsorption coverage onto LDHs particles and also the homogeneous distribution of active sites adsorbent (Lin et al., 2014). the isotherm was found to be linear studied by good correlation coefficient (R^2 =0.99). The data in Table 2 was showed the monolayer adsorption capacity Cobalt (II) have a higher value at 318 K using Mg/Al LDHs (36.855 mg/g).

Thermodynamic investigation plays an indispensable part in the prediction of adsorption mechanisms (i.e., physical or chemical). thermodynamic parameters (ΔG°, ΔH°, and ΔS°) can be calculated according to the thermodynamic laws through the following equations:

$$\Delta G = -RT \ln Kc \tag{7}$$

then, the relationship between thermodynamics parameter written by:

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

The Van't Hoff equation was obtain by Equation (7) and (8):

$$\ln Kc = \frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \tag{9}$$

The Gibbs energy was calculated by Equation (7), then the enthalpy (ΔH) and the entropy (ΔS) were obtained from a plot of lnKc versus 1/T, the plot were determined slope and intercept (Equation (9)). In this study the Kc derived from the Langmuir constant (KL) was employed for calculation of the thermodynamic parameters.

The thermodynamic parameters for adsorbing Cobalt (II) onto the Mg/Al and Ca/Al LDHs respectively were showed in Table 3. Table 3 were showed the negative values of ΔG were investigated the adsorption was spontaneously. Meanwhile, the positive ΔH reflects the endothermic nature of the adsorption process and the equilibrium constant (Table 3) at a higher temperature. Additionally, the positive ΔS values suggest that an increase in irregularity on the surface with several structural changes both adsorbate and adsorbent. In addition, when the adsorbate is adsorbed on the surface sites, the adsorbate replaces several molecules of water which is its can increasing the entropy.

Table 3. Values of Thermodynamic Parameters for The Adsorption of Cobalt (II) By Mg/Al and Ca/Al LDHs

T (K)	Concentration (mg/L)	Mg/Al ΔG (kJ/mol)	Mg/Al ΔS (J/mol.K)	Mg/Al ΔH (kJ/mol)	Ca/Al ΔG (kJ/mol)	Ca/Al ΔS (J/mol.K)	Ca/Al ΔH (kJ/mol)
303	10	-4.712	85.806	21.286	-1.005	69.614	21.666
308		-6.429			-2.384		
313		-8.145			-3.736		
318		-8.784			-3.943		
303	20	-2.762	111.236	37.480	-0.199	84.261	33.365
308		-5.049			-1.104		
313		-7.336			-2.008		
318		-8.309			-3.489		
303	30	-1.381	114.342	31.883	-0.245	96.094	42.864
308		-4.823			-1.175		
313		-8.265			-2.105		
318		-8.905			-4.997		
303	50	-0.231	138.846	44.383	-0.378	110.654	58.418
308		-0.463			-0.984		
313		-3.248			-1.591		
318		-4.567			-3.856		
303	80	-0.672	172.093	50.761	-0.378	122.035	78.148
308		-2.114			-0.984		
313		-3.082			-1.591		
318		-3.787			-2.345		

4. CONCLUSIONS

Adsorption process of cobalt (II) on layered double hydroxides Mg/Al and Ca/Al showed the adsorption rate 0.0053 min^{-1} and 0.0185 min^{-1}, respectively. Layered double hydroxides Mg/Al more reactive than layered double hydroxides Ca/Al. The adsorption kinetics investigation revealed that the adsorption of both dyes was followed the pseudo-second-order kinetics model. Isotherm parameters was calculated using Langmuir and Freundlich isotherm models. Based on adsorption data, Langmuir isotherm models more fitted than Freundlich, its indicated the adsorption was accour in monolayer adsorption coverage onto LDHs particles. The adsorption process was spontaneous and endothermic

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