Adsorptive Capacity of Malachite Green onto Mg/M^{3+} (M^{3+}=Al and Cr) LDHs

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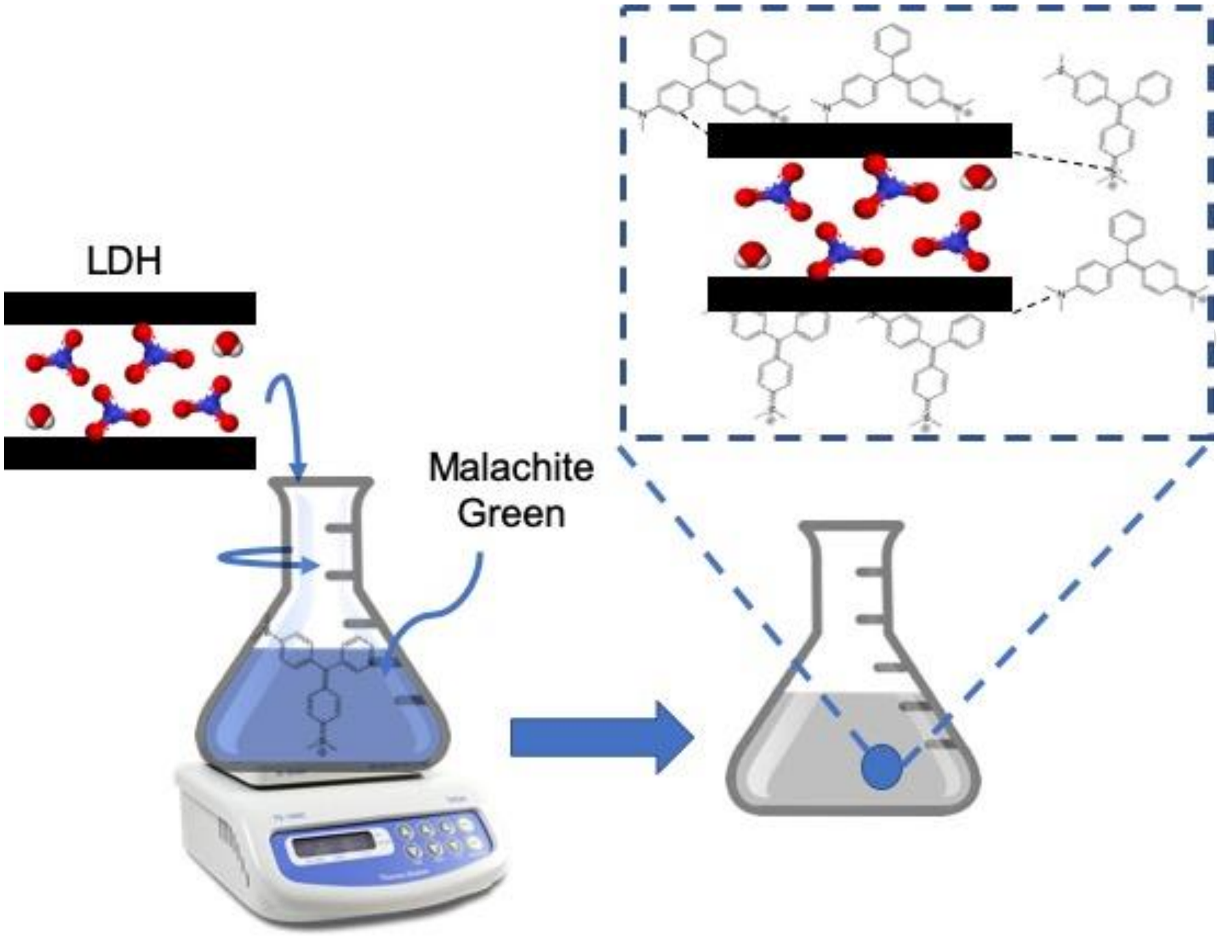
GRAPHICAL ABSTRACT



ABSTRACT

Layered double hydroxides (LDHs) of MgM^{3+} (M^{3+}=Al and Cr) were synthesized by coprecipitation method to form Mg/Al and Mg/Cr LDHs. The materials were applied as adsorbents of malachite green in aqueous solution. The physical properties of Mg/Al and Mg/Cr were analyzed using XRD, FTIR, BET and TGDTA characterizations. The XRD pattern shows the characteristic of LDHs which has diffraction at 11.47^0 (003) and at 34.69^0 (012) for Mg/Al and 12.45^0 (003) and at 38^0 (012) for Mg/Cr. The interlayer spaces of Mg/Al and Mg/Cr LDHs were 7.71 Å and 7.62 Å, respectively. The surface area of Mg/Al was higher than Mg/Cr. The FTIR spectra confirm that the intense peak at 1385 cm^{-1} denotes vibration of nitrate bond and M-O band in under 1000 cm^{-1}. Thus the Mg/Al and Mg/Cr LDHs were applied as adsorbents to remove malachite green in aqueous solution. The results of malachite green adsorption showed that malachite green was adsorbed onto Mg/Al and Mg/Cr followed pseudo second order and Langmuir adsorption parameter. The adsorption capacity of malachite green for Mg/Al and Mg/Cr was 44.444 mg/g and 33.784 mg/g, respectively. The thermodynamic study showed that the adsorption process was spontaneous, endothermic and favored in high temperature. The regeneration process showed that Mg/Al and Mg/Cr LDHs has high stability structure toward reusability of adsorbent until three cycles adsorption process.

Keywords: adsorption, layered double hydroxide, malachite green, Mg/Al, Mg/Cr

1. Introduction

Indonesian textile industries favored using reactive or synthetic dyes for dyeing the ethnic fabric and clothes (Islam *et al.*, 2019). The textile industry is wide source of organic pollutants such as dyes due to the highly variable mixtures of many polluting substances in wastewater (Sarma *et al.*, 2018). Many dyes are contained the aromatic structure and their character become high toxicity, undegradable and carcinogenic for human and also aquatic systems (Srivastava *et al.*, 2004). However, the synthetic dye colored can cover the surface of aquatic water and make the oxidation diffusion process by sunlight are reduced (Amran and Zulfikar, 2010). Furthermore, the ways to remove dyes from wastewater were studied such as adsorption, coagulation, filtration and photodegradation (Fu and Wang, 2011; Jarrah *et al.*, 2019). Among these methods, adsorption is suitable process due to easy, fast, cheap and non-toxic (Palapa, Taher, *et al.*, 2020). Malachite green is frequently used as synthetic dyes in several purposes. Malachite green (MG) is classified in the cationic dyestuff industry as a triarylmethane dye (Bennani Karim *et al.*, 2017). MG can be applied as an antimicrobial in aquaculture in low concentration but cause mortality of species in aquatic system (Tang *et al.*, 2012). Many researchers have been studied the adsorption of MG using several adsorbent such as activated carbon, hydrocharcoal, kaoline, zeolite and layered double hydroxides (Abdelrahman, 2018; Agarwal *et al.*, 2016).

Layered double hydroxides (LDHs) have been widely used as adsorbent due to high adsorption capacity, exchangeable ability and easy to prepare. According to Pareira et al (De Sá *et al.*, 2013) CaAl LDH had been used as adsorbent for yellow CFC and was obtained 0.88 mmol/g. Li et al.(Li *et al.*, 2017) also reported that CuAl LDH has ability to remove methyl orange in aqueous solution. On the other studies, CdAl LDH also reported as crystal violet adsorption and obtained 80% dye removal (Khan *et al.*, 2016). LDH is well-known as hydrotalcite, which is substituted by divalent and trivalent metal cation. The general formula of LDHs is $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}\ A_{x/n}^{n-} \bullet mH_2O$, where M is divalent and trivalent metal ions and $A_{x/n}^{n-}$ is interlayer anions with n valence (Sepehr *et al.*, 2017). There are many reported methods to prepare LDHs such as co-precipitation, sol-gel, hydrothermal and hydrolysis methods (Alibakhshi *et al.*, 2017). According to Bukhtiyarova (Bukhtiyarova, 2019) the mixing metal salts solutions at certain pH followed by aging with hydrothermal treatment was conducted to form LDHs. Lei et al (Lei *et al.*, 2017) revealed that the mixing cation salts were aging in 60-80^oC for longer times to form well-known layer structures. Hatami et al., (2018) reported that the hydrolysis treatment can produce ZnAl LDHs with high crystallinity particles.

In this work, MgM^{3+} (M^{3+}=Al and Cr) was used to form Mg/Al and Mg/Cr LDHs. Mg/Al and Mg/Cr LDHs were synthesized by co-precipitation methods and were applied as adsorbents of MG from aqueous solution. The physicochemical of adsorbent was characterized by XRD, FTIR, thermogravimetry, and surface area analyses. The adsorption study was determined by kinetic, isotherm, thermodynamic and regeneration studies.

2. Experimental Section

2.1. Chemical and instrumentation

The chemicals used in this research were $Mg(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich, 400.15 g/mol) $Al(NO_3).9H_2O$ (Sigma Aldrich, 375.13 g/mol), $Cr(NO_3)_3.9H_2O$ (Sigma Aldrich, 400.15g/mol), Cr(NO3)3•9H2O (EMSURE® ACS, Reag. Ph Eur, 256.41 g/mol), Na_2CO_3 (EMSURE® ACS, Reag. Ph Eur, 126.07 g/mol), (MallinckrodtAR®, 37%) , NaOH (EMSURE® ACS, Reag. Ph Eur, 40 g/mol) and HCl (MallinckrodtAR®, 37%). The X-ray diffraction (XRD) was conducted using a Rigaku Miniflex-6000 diffractometer. Sampel was scanned at 1 deg/min. The Brunauer–Emmett–Teller (BET) surface area was performed using a Quantachrome adsorption–desorption apparatus and the sample was degassed several times prior analysis. Fourier transform infrared (FTIR) was analyzed using a Shimadzu Prestige-21 spectrophotometer by KBr method. The sample was scanned at 400-4000 cm^{-1}. Analysis of MG was conducted using Biobase BK 1800 UV-Visible spectrophotometer at 619 nm.

2.2. Synthesis of MgAl and Mg/Cr LDHs

Mg/Al and Mg/Cr LDHs were synthesized by the co-precipitation method (Yanming *et al.*, 2017). Firstly, the solution of $Mg(NO_3)_2.6H_2O$ was mixed with $M^{3+}(NO_3)_3.9H_2O$ (3:1) (M^{3+} = Al, Cr) and stirred for 30 minutes. The solution of 1M Na_2CO_3 (Merck) and 2M NaOH were added to the reaction mixture. The mixture was mixed with continuous stirring until the precipitation formed and pH of the solution was adjusted to 10 by addition of sodium hydroxide solution. The reaction was kept at 80^0C for 24 hours to obtain Mg/M^{3+} (M^{3+}=Al and Cr) LDHs. The solid material was heated at 80 ^{o}C for 24 hours.

2.3. The effect of pH medium of MG by Mg/Al and Mg/Cr LDHs

The effect of pH medium on the adsorption was conducted using 0.05 L of 25 mg/L MG solution. The pH of medium was adjusted in the range 3-10 by addition of hydrochloric acid or sodium hydroxide solution. As much as 0.05 g of LDHs was added into MG solution under constant strirring at 230 rpm for 120 minutes. Then by using centrifugation at 3000 rpm the suspensions were separated and the concentration of MG on filtrate was determined by UV-Vis spectrophotometer.

2.4. Adsorption MG onto Mg/Al and Mg/Cr LDHs

As much as 1 g MG was dissolved with 1000 mL of water to obtain 1000 mg/L MG as dye stock solution. Standard curve of the MG solution was measure of each standard solution using spectrophotometer UV-Vis at 619 nm. The adsorption of MG were conducted in batch system. A 0.02 mg LDHs was added into 20 mL MG (Merck) with a concentration of 70 mg/L. The adsorption studies were carried out under stirring for different times (5-120 min) with optimum pH. After the stirring, the suspensions were separated using centrifugation at 3000 rpm for 10 minutes. The concentration of dye on filtrate was examined by UV-Vis spectrophotometer. The thermodynamic parameter were studied by varying initial concentration and temperatures. Then, as much as 0.5 g LDH was adsorbed with different concentrations (10-60 mg/L) and temperatures

(303-333 K) under the equilibrium time. The concentration of dye on filtrate was determined by UV-Vis spectrophotometer.

2.5. Desorption and Regeneration MG on Mg/Al and Mg/Cr LDHs

The desorption process was determined to examine the efficiency of the adsorbent. As much as 5 g LDHs were added with 50 ml MG and the mixture was stirred for 120 min. Then the concentration of MG on filtrate was determined by UV-Vis spectrophotometer. The adsorbent was dried for 2 hours. The residue (0.01 g) was mixed with each desorption reagents such as water, hot water, acetone, hydochlorid acid, and sodium hydroxide and stirred for 120 min. The filtrate was determined by UV-Vis spectrophotometer. The regeneration process was carried out after desorption by maximum reagent. The regeneration process was conducted in three cycles.

3. Results and Discussion

3.1. Adsorbent Characterization

The XRD patterns of Mg/Al and Mg/Cr LDHs are shown in Fig. 1. Two diffractions have similar patterns as presented the formation of well-ordered layered materials. The characteristic diffraction of LDHs was appeared at (003), (006), (009), (015), (110) and (113). Other peaks of Mg/Cr were found due to small impurities from synthetic condition. According to Palapa, *et al.*, (2020), the impurities can come from the high concentration of sodium hydroxide. This finding indicate that the formation of metal oxide. The d-spacing value has been calculated from Bragg equation resulted the interlayer space of LDHs. The interlayer spaces of Mg/Al and MgCr LDHs were 7.71 Å and 7.62 Å, respectively.

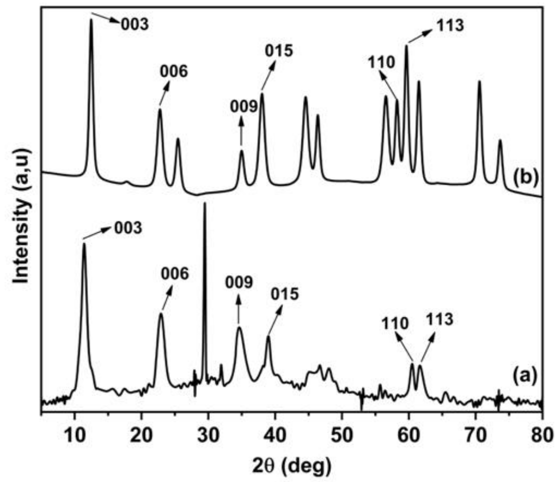


Figure 1. X-ray Powder diffraction patterns of Mg/Al (a) and Mg/Cr LDHs (b)

The FTIR spectrum of Mg/Al and Mg/Cr LDHs were shown in Fig. 2. The broad vibrations of hydroxyl group in bructite layer and interlayer space were confirmed at 3471cm^{-1} for both LDHs. The lower vibration at 1635 cm^{-1} is assigned as OH bending. The intense vibration at 1381 cm^{-1} indicated the N-O vibration from nitrate bending, which was located on interlayer space of LDHs. Thus, the metal oxide vibration was appeared at lower wavenumber below 800 cm^{-1}.

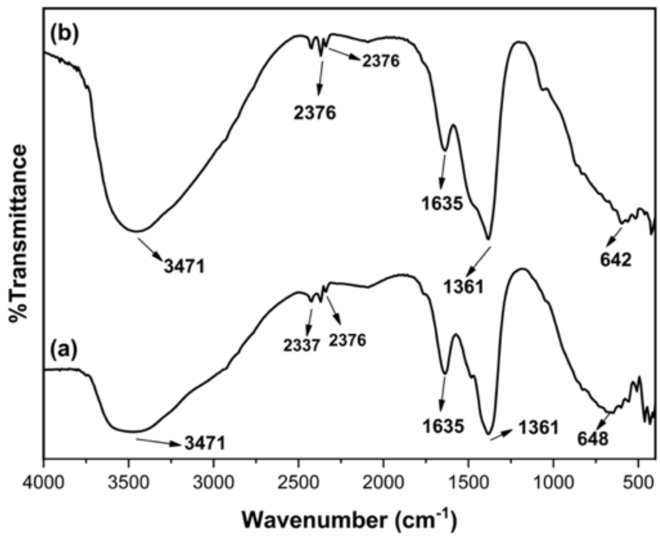


Figure 2. FTIR Spectrum of Mg/Al (a) and Mg/Cr LDHs (b)

The nitrogen adsorption-desorption isotherm of Mg/Al and Mg/Cr LDHs were shown in Fig. 3. The adsorption desorption curve showed that both materials have similar isotherm types and hysteresis.

This type belongs to type IV and H3, which denotes as mesoporous materials. However, the hysteresis loop of these materials showed the binding strength of anion in the interlayer space (Qu *et al.*, 2019). The calculated morphology properties using BET and BJH methods were listed in Table 1. The surface area of Mg/Al is higher than Mg/Cr. These results are probably due to the formation of metal oxide on Mg/Cr LDHs.

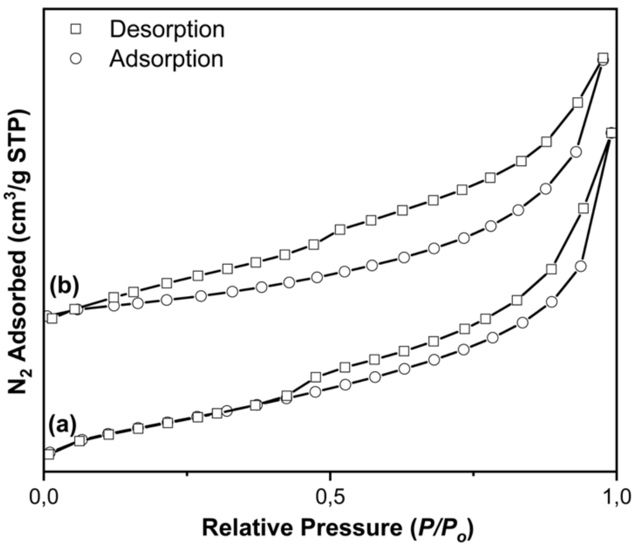


Fig. 3. Adsorption desorption nitrogen onto (a) Mg/Al and (b) Mg/Cr LDHs

Table 1. Morphology analysis of LDHs using BET and BJH method

Adsorbents	Surface Area (m^2/g)	Volume Pore (BJH) (cc/mg)	d-Pore (BJH)(nm)
Mg/Al	23.15	0.092	36.00
Mg/Cr	21.511	3.20	6.564

Furthermore, the thermogravimetry analysis of Mg/Al and Mg/Cr LDHs were shown in Fig. 4. Both LDHs have three decomposition peaks at 100 ^oC, 350 ^oC and 700 ^oC. Firstly, the decomposition at 100^oC was assigned as water loss in interlayer space of LDHs. The second decomposition was denoted as destruction of dihydroxylation of the brucite-like octahedral layers, and finally decomposition of interlayer of LDHs. At these stage the LDH's layer was break out as similar reported by (Samuei *et al.*, 2020).

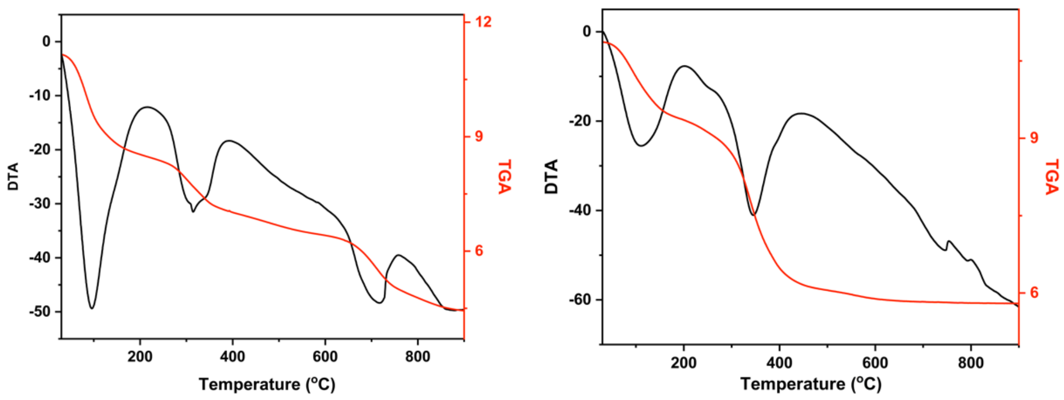


Fig. 4. Thermogravimetry pattern of (a) Mg/Al and (b) Mg/Cr LDHs

The stability of Mg/Al LDH and Mg/Cr LDHs were estimated by pH pzc as shown in Fig.5. The pH pzc was conducted to determine the charge of the materials. The cross point for both of LDHs were identified at 8 and 9 on Mg/Al and Mg/Cr, respectively. These pH values showed that LDHs have no charge. The pH below that points shows the positive charges and vice versa.

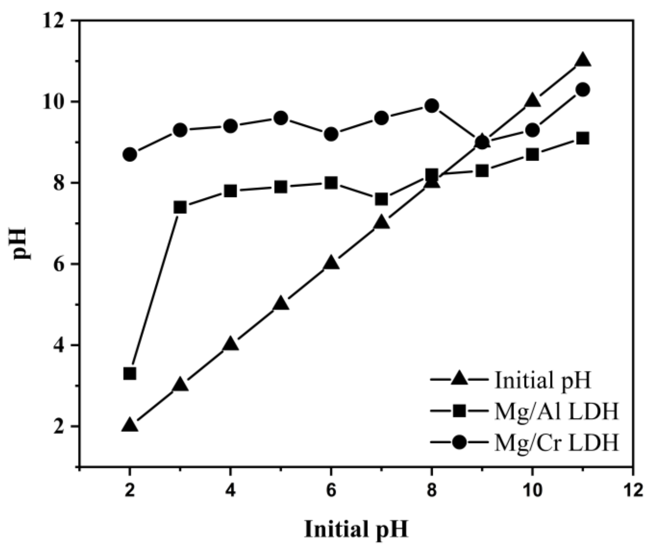


Fig.5. pHpzc of (a) Mg/Al and (b) Mg/Cr LDHs

The adsorption process of MG was also affected by pH as shown in Figure 6. The optimum pH was reached at 6 and 10 on Mg/Al and Mg/Cr LDHs, respectively. The maximum adsorption capacity is up to 80.2 mg/L for Mg/Al LDHs and 62.4 mg/L for Mg/Cr LDHs. Therefore the adsorption of MG for Mg/Al and Mg/Cr LDHs will be conducted at these optimum pH.

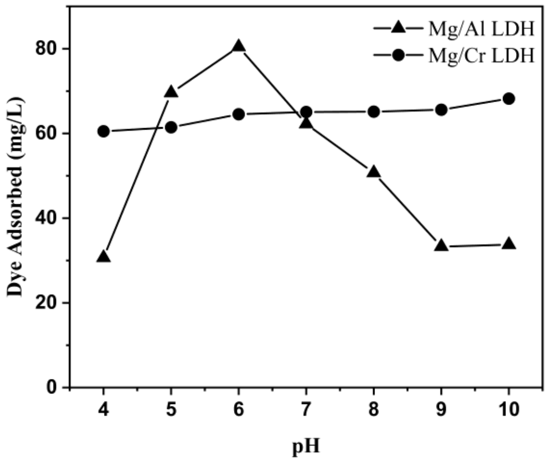


Fig.6. pH effect dye solution of adsorption MG by Mg/Al and Mg/Cr LDHs

3.2. Adsorption Study of MG onto Mg/Al and Mg/Cr LDHs

The adsorption study of MG onto Mg/Al and Mg/Cr LDHs was determined using several variables such as adsorption time, initial MG concentration, and temperature adsorption. The effect of adsorption time which was calculated using kinetic parameters were shown in Fig.6. Fig. 6 showed that the MG uptake increased rapidly with increasing adsorption time and reach equilibrium after 70 minutes. The adsorption kinetic was studied by pseudo first order (PFO) and second order (PSO) to predict the mechanism process on Mg/Al and Mg/Cr LDHs. The equations were presents as:

$\text{Log}(qe - qt) = \log qe - k_1 t/2.303$ (PFO) (1)

$t/qt = 1/k_2 qe^2 + 1/qe.t$ (PSO) (2)

with qe is dye adsorbed capacity (mg/g), and k is rate constant of PFO and PSO. The correlation of rate constant was determined using these equations and the results were listed in Table 2.

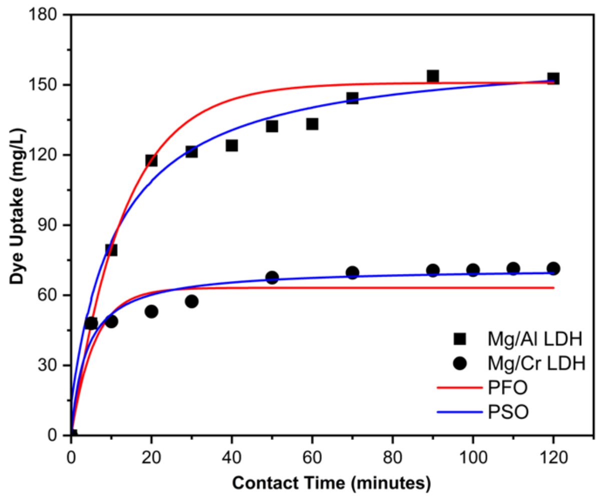


Figure 7. Time variation of adsorption of MG on Mg/Al (a) and Mg/Cr LDHs (b)

The results of kinetic parameter were obtained the coefficient correlation belong to PSO. This also supported by adsorbed dye capacity calculation (Qe_{calc}), which was closed to adsorbed dye capacity experiment ($Qe_{experiment}$). This indicate that the MG adsorption was following PSO kinetic model, which indicated the electrostatic attraction from adsorbate and adsorbent. In addition, the greater rate constant indicated that the adsorbate molecule become reactive (Sevim *et al.*, 2020).

Table 2. Kinetic parameters of dyes adsorption onto Mg/Al and Mg/Cr LDHs

Adsorbent	**MG Initial Concentration (mg/L)**	**$Qe_{experiment}$ (mg/g)**	**PFO**			**PSO**		
			Qe_{Calc} (mg/g)	**R^2**	**k_1**	**Qe_{Calc} (mg/g)**	**R^2**	**k_2**
Mg/Al	195.572	80.276	52.674	0.961	0.003	85.470	0.999	0.001
Mg/Cr	69.582	68.124	6.096	0.978	0.040	116.279	0.999	0.0089

The effect of equlibrium concentration in several temperatures was determined using adsorption isotherm Langmuir and Freundlich models. The Freundlich adsorption model was usually describe the multilayer and heterogeneous surface. The Langmuir is well-known as isotherm adsorption which described the interaction of adsorbate and adsorbent chemically (Zhang *et al.*, 2019).

Langmuir model was also known as monolayer adsorption/ one layer occupied in homogeneous surface. The equations was described as:

$Ce/qe = 1/qmax.Ce + 1/qmaxKL$ (Langmuir) (3)

$Ln\ qe = LnKF + 1/n\ Ln\ Ce$ (Freundlich) (4)

Where qmax and KL are Langmuir constant, KF and n are Freundlich constant with n giving an indication of favorable adsorption process and verify the type of adsorption process. The results of calculated parameters were listed in Table 3. The results indicated that the coefficient correlation closed to Langmuir than Freundlich and this findings indicated the adsorption process of Mg/Al and Mg/Cr LDHs are monolayer. The higher dye adsorbed capacities are 44.444 mg/g for Mg/Al and 33.784 mg/g for Mg/Cr LDHs.

Table 3. Isotherms parameter of adsorption of MG onto Mg/Al and Mg/Cr LDHs

LDHs	adsorption isotherm	adsorption constant	T(K)			
			303	313	323	333
Mg/Al	Langmuir	Q_{max}	10.000	15.432	11.696	44.444
		K_L	0.020	0.009	0.012	0.180
		R^2	0.414	0.645	0.633	0.715
	Freundlich	N	0.416	2.826	1.142	1.194
		K_f	77019	1.701	8.387	9.456
		R^2	0.866	0.748	0.996	0.996
Mg/Cr	Langmuir	Q_{max}	19.493	20.121	30.864	33.784
		K_L	0.111	0.137	0.209	0.272
		R_2	0.999	0.996	0.999	0.931
	Freundlich	N	1.131	1.146	2.324	2.518
		K_f	1.113	1.157	1.076	1.084
		R^2	0.999	0.999	0.999	0.905

The effect of temperature adsorption was described the thermodynamic parameter study. The thermodynamic parameter was obtained such as enthalpy (ΔH), entropy (ΔS) and Gibbs energy (ΔG). All adsorption condition was depended on temperature. Furthermore, Gibbs energy was calculated to determine the spontaneity and feasibility. The thermodynamic parameter was calculated using equation:

$$\ln KL = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

$$\Delta G^o = \Delta H - T\Delta S \quad (6)$$

Where T is temperature and R is the gas constant (Elmoubarki *et al.*, 2017). The calculated parameter was listed in Table 4. Table 4 showed the value of Gibbs energy was negative. Its means that the adsorption process was spontaneous. The decreases of Gibbs energy indicated that the adsorption process was more spontaneous and favored in high temperature. The value of entropy was described the randomness the adsorption process due to solid and solution interface. The positively value of enthalpy denotes the endothermic adsorption. The comparative adsorption capacities for MG showed in Table 5.

Table 4. Thermodynamic adsorption parameter of MG onto Mg/Al and Mg/Cr LDHs

Adsorbent	T (K)	Q_e (mg/g)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
Mg/Al	303	11.256	25.613	0.102	-5.272
	313	16.428			-6.291
	323	20.911			-7.310
	333	26.773			-8.330
Mg/Cr	303	76.579	5.955	0.030	-3.043
	313	78.432			-3.340
	323	79.287			-3.637
	333	80.237			-3.934

Table 5. Comparison of adsorption capacity of some adsorbents for MG removal

Adsorbent	**Adsorption Capacity (mg/g)**	**References**
Clay-biochar composite	12.125	(Fosso-Kankeu *et al.*, 2019)
MWCNT-COOH	11.73	(Rajabi *et al.*, 2016)
TiO_2	6.3	(Abou-Gamra and Ahmed, 2015)
Leucaena leucocephala	2.389	(Lee *et al.*, 2018)
Diatomite	23.64	(Tian *et al.*, 2016)
Co/Fe LDH	44.73	(Amin *et al.*, 2019)
Zn/Al LDH	126.6	(George and Saravanakumar, 2018)
Cu/Cr LDH	55.86	(Palapa, Mohadi, *et al.*, 2020)
Ni/Fe LDH	6.93	(Lesbani *et al.*, 2020)
Zn/Al LDH	60.7	(Mahmoud *et al.*, 2020)
Mg/Al LDH	44.444	This Study
Mg/Cr LDH	33.784	This Study

The desorption process was determined in order to examine about the molecule escapes from surface site of adsorbent (Shuang Zhang *et al.*, 2016). In our study, desorbed material was conducted by several reagents to examine a stability of material toward reusability process. Figure 8 presents the desorption study of MG onto MgAl and MgCr LDHs by several reagents. The largest percentage of desorption of MG was in the HCl solvent on MgAl LDHs (11.94%) and MgCr LDHs (13.84%). The regeneration of Mg/Al and Mg/Cr LDHs was investigated by three times cycles. The recycling process of LDHs adsorption-desorption was illustrated in Figure 9. The high effectivity of reuse material showed that the Mg/Al LDHs have good recycling properties than

Mg/Cr LDHs. This assumed that Mg/Al LDHs have good stacked layers sheet as uses. The decreases in removal efficiency from LDHs indicated that the cumulated dye adsorbed was trapped in interlayer space of LDHs (Palapa *et al.*, 2019).

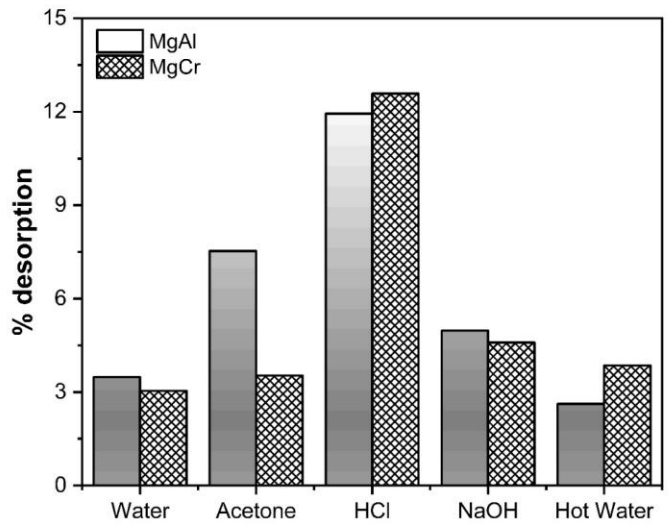


Figure 8. Desorption of MG on MgAl and Mg/Cr LDHs

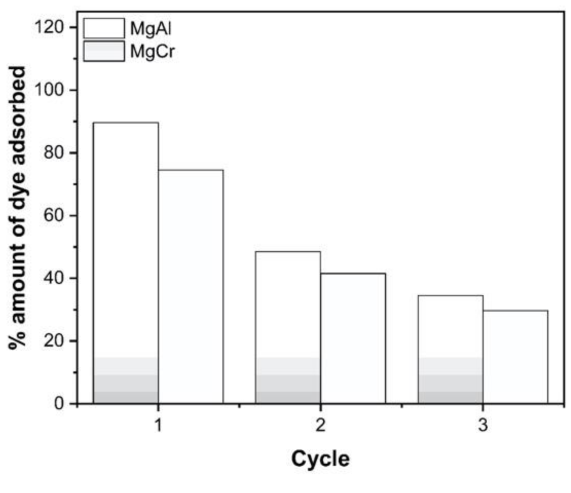


Figure 9. Regeneration of MG on MgAl and on Mg/Cr LDHs

4. Conclusion

In the presents research, MgM^{3+} LDHs (M^{3+}=Al and Cr) have been used as efficient adsorbent to remove MG from aqueous solution. The characterization of MgM^{3+} LDHs (M^{3+}=Al and Cr) was performed using XRD which is interlayer space of Mg/Al higher than Mg/Cr LDHs. The surface area analysis results showed that the Mg/Al LDHs has higher surface area than Mg/Cr LDHs. The kinetic parameter was indicated the adsorption mechanism follow PSO with supporting finding the qcalculation closed to qexperiment. However, the adsorption isotherm followed Langmuir isotherm model, which is the dye adsorbed capacity obtained 44.444 mg/g for Mg/Al LDHs and 33.784 mg/g for Mg/Cr LDHs. In addition, the regeneration process showed that Mg/Al LDHs has good reuseability properties than Mg/Al LDHs using HCl as desorbed's reagent.

Acknowledgement

The authors thank Universitas Sriwijaya for financial support of this research through Hibah Profesi 2020-2021 contract number 0687/UN9/SK.BUK.KP/2020 and also to Research Center of Inorganic Materials and Complexes FMIPA Universitas Sriwijaya for instrumental analysis.

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