

Mg/Cr-(COO)₂²⁻ layered double hydroxide for malachite green removal

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Abstract

Mg/Cr layered double hydroxide (LDH) was prepared and modified using an intercalation of oxalate anions ((COO)₂²⁻) to form Mg/Cr-(COO)₂²⁻. The materials were then investigated to malachite green removal to determine the adsorption ability. Furthermore, the desorption process and regeneration of adsorbent were systematically conducted. The adsorption of green malachite on Mg/Cr- LDH and Mg/Cr-(COO)₂²⁻ materials fitted to the pseudo-second-order (PSO) kinetic model and Freundlich isotherm model with an adsorption capacity of 33.784 mg/g (333K) for Mg/Cr LDH and 64.516 mg/g (333K) for Mg/Cr-(COO)₂²⁻. Thermodynamic data showed that the adsorption process was spontaneous and endothermic. Also, the appropriate reagent desorption study was found as hydrochloric acid and material regeneration studies exhibited a good recycling performance after 3 times cycles and, the Mg/Cr-oxalate showed a good performance for malachite green adsorption. It can be concluded that Mg/Cr--(COO)₂²⁻ can adsorb the dye stuffs effectively.

Keywords: Mg/Cr; oxalate; intercalation; adsorption; malachite green

1. Introduction

Synthetic dyes commonly are used widely in industrial applications for having an advantage of providing bright colors, being durable [1], being simple to apply [2], and economical [3]. In this decade, the use of synthetic dyes has been on the rise in the textile industry. However, colored textile waste causes some environmental problems because the chemical structure of dye is stable in water and covers all aquatic environmental systems [2]. Synthetic dyes are toxic, mutagenic, carcinogenic, and teratogenic [1,3]. Thus, the removal of synthetic dyes from the solution is deemed crucial. Various wastewater treatment methods can be carried out to remove dyes such as oxidation, coagulation [4], flocculation [5], membrane filtration [6], ion exchange [7], and adsorption [8].

Of these methods, adsorption is considered to be the most common process due to its fast process and effectiveness [4,7]. The effectivity adsorption process is strongly dependent upon the properties and quality of the adsorbent. Various materials can be used for adsorbents in the dye adsorption process such as rice husks [7], activated carbon [6], chitosan [9], apple peel [10], coconut shell [11], kaolin, montmorillonite [12] and layered double hydroxide [13].

Layered double hydroxide is also known as hydrotalcite or anionic clay [14]. It can be used as a catalyst, ion exchanger and adsorbent and has the following general formula $[M^{2+}1-xM^{3+}x(OH)_2]^{x+}[A^{n-}x/n.mH_2O]$ where M^{2+} and M^{3+} are the valency of metals, x is molar ratio and A^{n-} is anion in interlayer [15]. The characteristic of layered double hydroxide is flexibility where the anions in the interlayer can be exchanged dependent upon the application of layered double hydroxide [16]. One of the anions that can be exchanged is the oxalate anion [17], which aims to increase the interlayer distance [16].

According to Palapa et al., (2020) [18] the adsorption of malachite green dyes was performed using layered double hydroxide Cu/M³⁺ (M³⁺ = Al, Cr) with a q_{max} of 59.523 mg/g and 55.865 mg/g, respectively. Ascii, 2016 [19] reported the removal of the dye Congo red and indigo carmine using layered double hydroxide Mg-Al-Cl. Meanwhile, Doungmo et al., (2016) [17] reported that the intercalation of oxalate ions on layered double hydroxide MgAl used for the adsorption of nickel ions had an adsorption capacity of 1310 mg/g. Palapa et al., 2020 [8] reported Cu/Al LDH intercalated with polyoxometalate anion was used for the adsorption of malachite green with the adsorption capacity of 55.866 mg/g and 149.253 mg/g, respectively. Darmograi et al., 2015 [20] reported the adsorption of methyl orange, orange II, and orange G using layered double hydroxide intercalated with MgAl. Thus, Taher et al., 2019 [16] reported that the intercalation of Ca/Al layered double hydroxide with the Keggin anion was

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used as an adsorbent of cadmium (II) ion. The adsorption capacity was greater than the one before the intercalation process. Of all these studies, the LDH intercalated with oxalate anion has been conducted as an adsorbent of other adsorbates but it still had limitation. Thus, in this research the ability of adsorption capacity by LDH-oxalate intercalation material was tested.

For this research, Mg/Cr LDH was synthesized by means of using the co-precipitation method before being intercalated with oxalate anion to form Mg/Cr-(COO)₂²⁻ as an adsorbent of malachite green. This research conducted MgCr LDH intercalated by oxalic anion, which has a good characterization; however, some researchers are not so interested in since these materials still have a small surface area. Therefore, we conducted the modification (intercalation) process to get a large surface area of LDH. Materials were characterized using XRD analysis, and material surface area analysis was carried out by BET nitrogen adsorption-desorption method and identification functional group using FT-IR. Malachite green is one of the cationic dyes, which cannot be degraded in nature. Figure 1 shows the structure of the malachite green dye. To determine the adsorption study, we conducted the variation of adsorption time, malachite green concentration and adsorption temperature aimed to determine the kinetic and thermodynamic parameter models and isotherm parameter was systematically conducted. The desorption study was tested using several reagents aimed to determine the reagent with the optimum desorption conditions of malachite green and the regeneration study was carried out in three cycles.

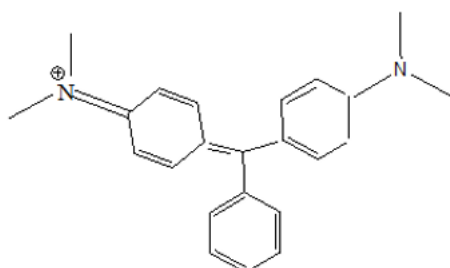


Fig. 1. Chemical structure of malachite green

2. Materials and Methods

2.1. Chemicals and Instrumentation

All chemicals were obtained by Sigma Aldrich without purification such as Mg(NO₃)₂·6H₂O, Cr(NO₃)₃·9H₂O, Na₂CO₃, NaOH; HCl 37% by MallinckrodtAR[®], and H₂C₂O₄·2H₂O by EMSURE[®] ACS, Reag. Ph Eur. The characterization of materials was conducted using XRD Rigaku miniflex-6000, FT-IR Shimadzu Prestige-21, BET Quantachrome Micrometric ASAP and Spectrophotometer UV-Visible Biobase BK-UV 1800 PC at 617 nm.

2.2. Synthesis of Mg/Cr LDH

Mg/Cr LDH was prepared by pH 10 and co-precipitation method. 100 mL Mg(NO₃)₂·6H₂O 0.75 M was mixed with Cr(NO₃)₃·9H₂O 0.25 M in a beaker. Na₂CO₃ 1 M 100 mL was added to the mixture and 2 M NaOH as much as 50 mL until it reached pH 10 and stirred at a temperature of 80°C for 24 hours.

2.3. Preparation of Mg/Cr-(COO)₂²⁻

The intercalation of Mg/Cr LDH material with (COO)₂²⁻ was prepared using ion-exchange method. It was carried out by mixing 5 g of Mg/Cr LDH and 100 mL of water and stirring for 60 minutes under N₂ gas flow. The mixture was then added with an oxalic acid (25 mL, 2 M) solution and pH was adjusted to 9 using a solution of NaOH before the mixture was stirred for 24 hours. The precipitate was filtered, washed, and dried at 100°C for 24 hours to obtain Mg/Cr-(COO)₂²⁻.

2.4. Removal experiments

First, the effect of adsorption time was carried out using a 70 mg/L concentration of malachite green dye, which was put into a 25-mL beaker. Further, 25 mg of adsorbent was added and stirred in the range at 5-120 minutes. Subsequently, the effect of malachite green concentration and temperature were carried out with the concentration of malachite green of 50 mg/L, 60 mg/L, 80 mg/L, 90 mg/L, and 100 mg/L taken as much as 25 mL and then put into a beaker and 25 mg of adsorbent was added. Then, the mixture was stirred with the influence of the adsorption temperature at 303 K, 313 K, 323 K, 333 K. After stirring, the suspension was separated using a centrifuge and the concentration of malachite green on the solution was tested at the maximum wavelength malachite green of 617 nm.

The kinetics study was examined using pseudo-first-order (PFO) (1) and pseudo-second-order (PSO) (2); the isotherm parameters examined using Langmuir (3) and Freundlich (4); and the thermodynamic (5) parameter. The formula should be written by:

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2,303} \right) t \quad (1)$$

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

$$\frac{C}{m} = \frac{1}{bKML} + \frac{C}{b} \quad (3)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

$$\ln K_{eq} = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \quad (5)$$

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

2.5. Desorption and Regeneration Experiments

The percentage of adsorbed dye, the formula should be written by:

$$\% D = \frac{C_{ads}}{C_{dsp}} \times 100\%$$

The regeneration efficiency was determined using the equation:

$$\% \text{ regeneration} = \frac{Q_r}{Q_0} \times 100 \%$$

The desorption of malachite green was tested by 50 mL of malachite green with a concentration of 100 mg/L before being added with 1g of LDH and stirred for 2 hours. The used adsorbent was then dried, and after drying the residue was taken as much as 10 mg added to 10 mL of reagents (HCl, water, NaOH, hydroxylamine, and Na-EDTA) and stirred for 2 hours. Thus, the regeneration process carried out by desorbed materials adsorbed a malachite green dye (50 mL, 100 ppm). The mixture was stirred for 2 hours as well. Then, the adsorbent was dried at room temperature. The dry residue was used for the desorption process by adding 25 mL of 0.01 M HCl and stirring for 2 hours. The residue was then dried and after drying it was reused in the same procedure.

3. Results and Discussion

Figure 2 shows the characterization of Mg/Cr LDH and Mg/Cr-Oxalate LDH using the XRD powder analysis. The materials of Mg/Cr LDH had diffraction peaks at 11° (003), 22° (006), 36° (015), and 60° (110). According to Mandal et al., [21] a sharp and symmetrical diffraction pattern indicates that the material is crystalline. Layered double hydroxide was characterized as the peaks with planes (003), (006), (018), (110), and (113) indicating that layered structure was well-formed. The diffraction peak at 11.97° had the interlayer distance of 7.62 Å. The interlayer distance of Mg/Cr LDH can be increased by exchanging nitrate ions with oxalate ions on the interlayer. The diffraction peaks of Mg/Cr-LDH after intercalation showed a diffraction pattern similar to that of Mg/Cr LDH. Mg/Cr-Oxalate LDH had a diffraction peak at 11.35° with interlayer distance of 10.21 Å. The increase of interlayer gallery was 2.59 Å because oxalate ions entered interlayer and replaced nitrate ions.

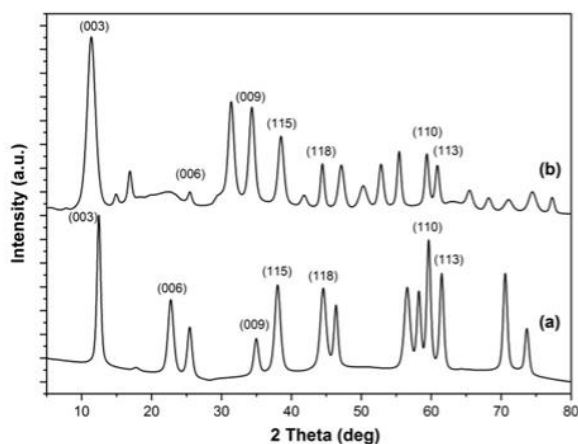


Fig. 2. XRD patterns of Mg/Cr (a) and Mg/Cr-(COO)₂²⁻ (b)

Figure 3 shows the nitrogen adsorption-desorption analysis on Mg/Cr and Mg/Cr-(COO)₂²⁻. As shown in figure 3, the hysteresis occurred in the graph showed the presence of pores in the material. Isotherm graph showed that material Mg/Cr and Mg/Cr-(COO)₂²⁻ followed the type IV isotherm model. According to Moller and Adrij (2017) [22], type IV isotherm shows the hysteresis of mesoporous materials.

Table 1 presents the BET analysis data showing that Mg/Cr-(COO)₂²⁻ had a surface area twice larger than that of Mg/Cr-LDH. There was an increase in surface area of 26.115 m²/g after intercalation process of oxalate ions. In contrast, the pore

size and pore volume were inversely proportional to the surface area. The pore size and pore volume of Mg/Cr were greater than that of Mg/Cr-(COO)₂²⁻. This occurred due to the opening or addition of Mg/Cr-(COO)₂²⁻ LDH material interlayered distance, so the pore size and pore volume in the Mg/Cr-(COO)₂²⁻ LDH became smaller and were covered by the size of the oxalate ion [23].

Table 1. Adsorbents properties

Materials	S _{area} (m ² /g)	P _{size} (nm), BJH	V _{pore} (cm ³ /g) _{BJH}
Mg/Cr	21.511	3.20	6.564
Mg/Cr-(COO) ₂ ²⁻	49.270	0.158	6.511

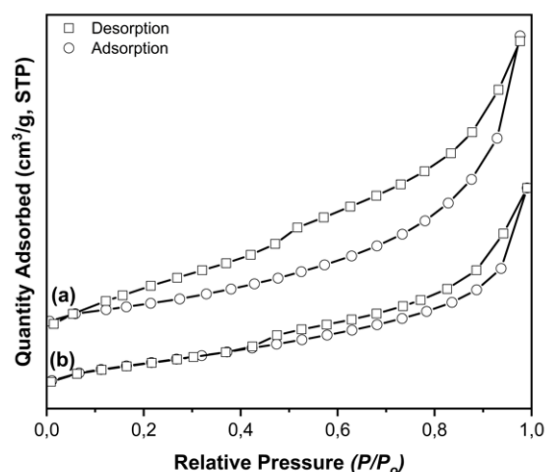


Fig. 3. BET curve Mg/Cr (a) and Mg/Cr-(COO)₂²⁻ (b)

Figure 4 shows the FT-IR spectra of Mg/Cr and Mg/Cr-(COO)₂²⁻ LDH. Mg/Cr LDH and Mg/Cr-(COO)₂²⁻ LDH had the widened peaks of around 3448 cm⁻¹ indicating the -OH stretching vibration. The peaks at 1635 cm⁻¹ (figure 4a) and 1643 cm⁻¹ (figure 4b) showed the -OH bending vibrations of water molecules. Vibration at 1381 cm⁻¹ indicated the presence of nitrate ion from Mg/Cr and Mg/Cr-(COO)₂²⁻ and vibrations at 956-771 cm⁻¹ indicated the presence of M-O [24] [25]. According to Arco et al (2003) [26], the vibrations at the peaks of 1385 cm⁻¹ and 1261 cm⁻¹ indicate the presence of C-O from oxalate. The intensity of the nitrate peak decreases due to ion exchange as shown in figure 4b. The oxalate anion replaced the nitrate ion on the Mg/Cr-(COO)₂²⁻.

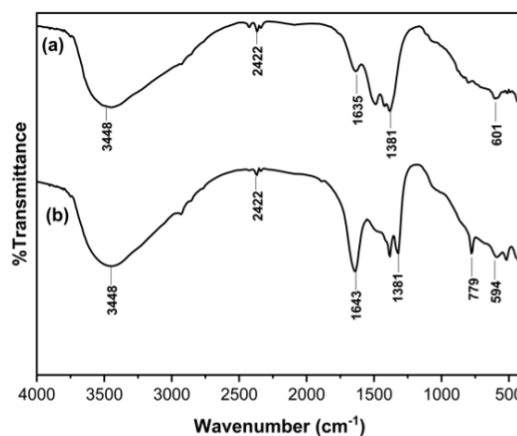


Fig. 4. FT-IR Spectrum of Mg/Cr (a) and Mg/Cr-(COO)₂²⁻ LDH (b)

Firstly, the kinetic parameter was determined by the variation of the adsorption contact times between adsorbate and adsorbent. Figure 5 and Table 2 show the effect of contact time on the adsorption of malachite green using Mg/Cr and Mg/Cr-(COO)₂²⁻ LDH. The adsorption of malachite green increased with the increasing adsorption contact time. The results showed that adsorption of malachite green on Mg/Cr-(COO)₂²⁻ was slightly higher than Mg/Cr LDH. These adsorption results were equal to XRD and BET analyses. The XRD characterization showed that Mg/Cr-(COO)₂²⁻ had a greater interlayer distance than Mg/Cr LDH. BET analysis also showed that the Mg/Cr-(COO)₂²⁻ had a larger surface area than Mg/Cr LDH. Furthermore, figure 5 shows the adsorption of malachite green with Mg/Cr LDH adsorbent reached the adsorption equilibrium after the adsorption time of 70 minutes while the Mg/Cr-(COO)₂²⁻ LDH adsorbent reached a shorter adsorption equilibrium after 30 minutes of adsorption process.

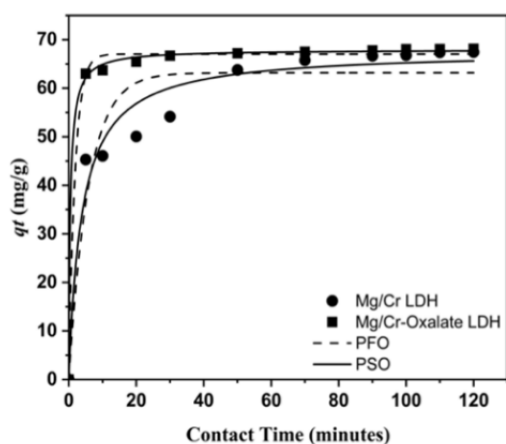


Fig. 5. Time variation of adsorption malachite green onto Mg/Cr LDH and Mg/Cr-Oxalate LDH

Table 2 shows that the adsorption of malachite green on Mg/Cr and Mg/Cr-(COO)₂²⁻ as adsorbents followed the PSO kinetic model (based on R²). The k₂ value of Mg/Cr-(COO)₂²⁻ was smaller than that of Mg/Cr LDH. This indicated that the Mg/Cr LDH was slightly more reactive than the Mg/Cr-(COO)₂²⁻. Malachite green adsorption with Mg/Cr LDH had q_e of 57.126 mg/g while Mg/Cr-(COO)₂²⁻ had q_e of 68.124 mg/g. Thus, the results of the kinetic parameter for the Mg/Cr-(COO)₂²⁻ LDH showed that q_e of malachite green was greater than the Mg/Cr LDH.

Secondly, variations in the malachite green concentration and temperature of the adsorption process that described the equilibrium of the adsorption process are shown in figure 6a and 6b. It can be observed that there was an increase in adsorption of malachite green along with the increase in concentration of malachite green and temperature on the adsorption process. The adsorption of malachite green for Mg/Cr and Mg/Cr-(COO)₂²⁻ LDH as adsorbents showed that the adsorption of dye on Mg/Cr-(COO)₂²⁻ LDH was greater than that of Mg/Cr-LDH.

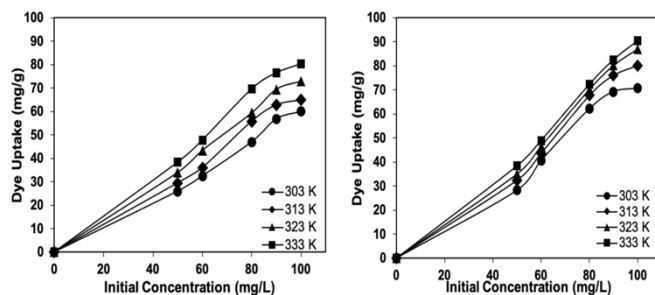


Fig. 6. Concentration vs. malachite green uptake of Mg/Cr (a) and Mg/Cr-(COO)₂²⁻ (b)

Table 3 shows that the removal of malachite green followed the Freundlich isotherm model rather than the Langmuir isotherm model, as seen from the correlation coefficient close to 1 (R² > 0.932). According to Chung et al (2015) [27] Freundlich isotherm is assumed to be a multilayer adsorption process and the amount of adsorbed gradually increases. Freundlich isotherm describes the characteristics of the adsorption process for heterogeneous surfaces [28]. Table 3 shows the increase in adsorption maximum capacity with the increasing temperature of the adsorption process. The adsorption maximum capacity (Q_{max}) of malachite green adsorption for Mg/Cr and Mg/Cr-(COO)₂²⁻ LDH obtained 33.784 mg/g (333K) and 64.516 mg/g (333K), respectively. The q_e for Mg/Cr-(COO)₂²⁻ LDH was found greater than pristine making the intercalation had a larger surface area. Based on the literature study we conducted, this research showed a good ability for adsorption malachite green better than Mn/Fe LDH coating by polyethersulfone with the adsorption capacity of 13.49 mg/g [29]; CuCr-Polyoxometalate was conducted to remove malachite green with adsorption capacity 55 mg/g [11]; Sulfur-doped biochar had adsorption capacity of 30.18 mg/g [30]. Of all this study, the Mg/Cr-(COO)₂²⁻ was found to have a good ability for adsorption malachite green in aqueous solution.

Thermodynamic parameters of malachite green adsorption for Mg/Cr LDH and Mg/Cr-(COO)₂²⁻ LDH as adsorbents such as ΔH (enthalpy), ΔS (entropy), ΔG (Gibbs free energy) are shown in Table 4 and 5.

Table 4 and 5 present that the removal of malachite green on Mg/Cr and Mg/Cr-(COO)₂²⁻ LDH as adsorbents occurred spontaneously, as indicated by negative ΔG. The ΔH value in the range ΔH < +40 kJ/mol indicated that the adsorption of malachite green occurred physically and endothermic. [31], correlated with the adsorption isotherm data as presented in Table 3 following the Freundlich isotherm model. The ΔS value increased after the Mg/Cr LDH process was intercalated, indicating that the degree of irregularity increased for the adsorption of malachite green [8]. According to [27],

adsorption temperature might result in physisorption. These phenomena indicated that the viscosity of solvent and malachite green would lead to the mobility of the solute at higher temperatures and cause the adsorption to be more favorable at high temperatures [11].

Table 2. Kinetic study malachite green removal

Adsorbent	Q _e ^{experiment} (mg/g)	PFO			PSO		
		Q _e ^{Calc} (mg/g)	R ²	k ₁	Q _e ^{Calc} (mg/g)	R ²	k ₂
Mg/Cr LDH	57.126	35.925	0.955	0.058	16.891	0.999	0.059
Mg/Cr-(COO) ₂ ²⁻	68.124	6.095	0.978	0.040	40.224	0.999	0.008

Table 3. Kinetic study of Mg/Cr LDH and Mg/Cr-oxalate LDH

adsorbents	Adsorption Isotherm	Adsorption Constant	T (K)			
			303	313	323	333
Mg/Cr	Langmuir	Qmax	19.493	20.121	30.864	33.784
		kL	0.111	0.137	0.209	0.272
		R ²	0.999	0.996	0.999	0.932
	Freundlich	n	1.131	1.146	2.324	2.518
		kF	1.113	1.157	1.076	1.084
Mg/Cr-Oxalate	Langmuir	Qmax	23.685	81.031	64.053	64.516
		kL	0.001	0.002	0.035	0.062
		R ²	0.999	0.999	0.969	0.976
	Freundlich	n	0.029	0.140	0.140	0.871
		kF	1.641	1.132	2.003	1.262
R ²	0.999	0.983	0.994	0.999		

Table 4. Thermodynamic parameter of adsorption malachite green onto Mg/Cr LDH

Concentration (mg/L)	T (K)	Q _e (mg/g)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
50	303	26.556	7.976	0.028	-0.398
	313	28.932			-0.675
	323	29.597			-0.951
	333	30.191			-1.228
60	303	36.627	4.591	0.019	-1.096
	313	37.434			-1.284
	323	38.242			-1.472
	333	38.931			-1.660
80	303	47.245	2.530	0.014	-1.729
	313	47.316			-1.870
	323	48.029			-2.010
	333	48.575			-2.151
90	303	66.793	9.202	0.039	-2.747
	313	70.214			-3.141
	323	71.306			-3.536
	333	72.161			-3.930
100	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. Thermodynamic parameter of adsorption malachite green onto Mg/Cr LDH

Concentration (mg/L)	T (K)	Q _e (mg/g)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
50	303	27.055	27.991	0.094	-0.481
	313	32.447			-1.420
	323	35.060			-2.360
	333	38.433			-3.300
60	303	40.617	19.642	0.071	-1.796
	313	43.658			-2.504
	323	45.914			-3.211
	333	48.765			-3.919
80	303	61.046	22.796	0.091	-4.640
	313	63.160			-5.545
	323	65.155			-6.451
	333	66.010			-7.356
90	303	75.392	15.436	0.065	-4.113
	313	77.767			-4.758
	323	79.287			-5.403
	333	81.104			-6.048
100	303	82.660	19.730	0.078	-3.878
	313	84.917			-4.658
	323	87.862			-5.437
	333	90.475			-6.216

The desorption studies of the malachite green on adsorbent were carried out with several reagents as shown in figure 7. The results in figure 7 showed that the hydrochloric acid reagent desorb malachite green more than the other reagents. This was because the H⁺ ions from HCl were able to release the anions of malachite green through the interaction between HCl and the adsorbent. thus, the desorption process also indicated the way of the interaction of malachite green to Mg/Cr-(COO)₂²⁻. The high desorption using hydrochloric acid indicated the interaction of van der Waals and the chemical bond between dye and adsorbent molecule. Mg/Cr was more desorbed of malachite green dye than Mg/Cr-(COO)₂²⁻ LDH. This assumption indicated that malachite green was more trapped on the active site of Mg/Cr than Mg/Cr-(COO)₂²⁻ LDH. Also, LDH can be exfoliated if the concentration of hydrochloric acid is so high. This finding is also supported by the ΔH of the adsorption process.

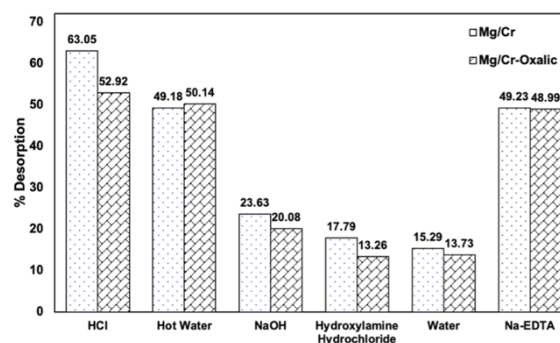


Fig. 7. Desorption malachite green on Mg/Cr LDH and Mg/Cr-Oxalate LDH

The adsorbent regeneration was carried out using HCl as a desorption reagent to release the malachite green after the adsorption process.

The regeneration study carried out by a three cycles as shown in figure 8. The adsorption efficiency of malachite green using Mg/Cr and Mg/Cr-(COO)₂²⁻ LDH adsorbents for the regeneration process was decreased. The amount of malachite green adsorption at first regeneration on Mg/Cr and Mg/Cr-(COO)₂²⁻ was 46.22% and 50.19%, respectively. The adsorption at second regeneration was 38.13% for Mg/Cr LDH and 41.65% for Mg/Cr-(COO)₂²⁻ and was smaller in third regeneration process. The adsorption effectivity of the Mg/Cr-

(COO)₂²⁻ LDH had higher adsorption compared to Mg/Cr LDH toward regeneration adsorbent. These phenomena were related to the exfoliation of LDH structure by acid during the desorption process [32].

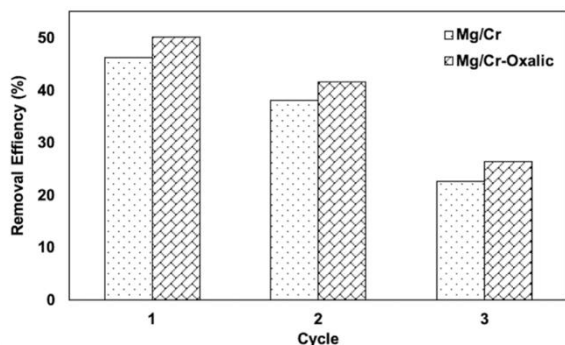


Fig. 8. Regeneration of malachite green on Mg/Cr LDH and Mg/Cr-(COO)₂²⁻ LDH

4. Conclusion

Mg/Cr LDH was successfully synthesized with (COO)₂²⁻ to form Mg/Cr-(COO)₂²⁻ LDH was conducted by increasing the interlayer distance by 2.59 Å and surface area 49.270 m²/g. Removal study of malachite green used Mg/Cr and Mg/Cr-(COO)₂²⁻ LDH had the adsorption capacity of 33.784 mg/g and 64.516 mg/g, respectively. The adsorption capacity of malachite green increased twice from pristine. The adsorbent regeneration process showed the ability of Mg/Cr and Mg/Cr-(COO)₂²⁻ LDH to recycle after three times and effective to remove malachite green from wastewater.

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