Mg/Cr-(COO)$_2$ layered double hydroxide for malachite green removal

Neza Rahayu Palapa$^{a,d}$, Arini Fousty Badri$^b$, Mardiyanto$^e$, Risfidian Mohadi$^a$, Tarmizi Taher$^e$, Aldes Lesbani$^{b,d,*}$

$^a$Department of Chemistry Faculty of Mathematics and Natural Science, Universitas Sriwijaya, Palembang, 30662, Indonesia
$^b$Graduate School Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Palembang, 30139, Indonesia
$^c$Department of Environmental Science, Institut Teknologi Sumatera, Lampung, 35365, Indonesia
$^d$Research Center of Inorganic Material and Complexes Faculty of Mathematics and Natural Science, Universitas Sriwijaya, Palembang, 30662, Indonesia
$^e$Department of Pharmacy, Faculty of Mathematics and Natural Science, Universitas Sriwijaya, Palembang, 30662, Indonesia

Abstract

Mg/Cr layered double hydroxide (LDH) was prepared and modified using an intercalation of oxalate anions ((COO)$_2^-$) to form Mg/Cr-(COO)$_2$. 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)$_2$ 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)$_2$. 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)$_2$ 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 effectiveness 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 $[\text{M}^{2+}]_x\text{X}^{x-}x\text{(OH)}_2]^{x+} [\text{A}^{n-}\text{solv}m\text{H}_2\text{O}]$ where $\text{M}^{2+}$ and $\text{M}^{3+}$ are the valency of metals, $x$ is molar ratio and $\text{An}^{-}$ 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/Al (M$^{3+}$ = Al, Cr) with a $q_{\text{max}}$ 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, Dooungmo 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...
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)$_2^{2-}$ 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](image)

2. Materials and Methods

2.1. Chemicals and Instrumentation

All chemicals were obtained by Sigma Aldrich without purification such as Mg(NO$_3$)$_2$·6H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, Na$_2$CO$_3$, NaOH; HCl 37% by MallinckrodtAR, and H$_2$C$_2$O$_4$·2H$_2$O by EMSURE® ACS, Reag. Ph Eur. The characterization of materials was conducted using XRD Rigaku miniflex-6000, FT-IR Shimadzu Prestige-21, BET Quantachrome Micrometic 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(NO$_3$)$_2$·6H$_2$O 0.75 M was mixed with Cr(NO$_3$)$_3$·9H$_2$O 0.25 M in a beaker. Na$_2$CO$_3$ 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)$_2^{2-}$

The intercalation of Mg/Cr LDH material with (COO)$_2^{2-}$ 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 N$_2$ 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)$_2^{2-}$.

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:

\[
\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t
\]

\[
\frac{c}{m} = \frac{1}{bkML} + \frac{c}{b}
\]

\[
\log q_e = \log K_F + 1/n \log C_0
\]

\[
\ln K_F = \frac{\Delta S}{R} + \frac{\Delta H}{RT}
\]

\[
\Delta G = \Delta H - T\Delta S
\]

2.5. Desorption and Regeneration Experiments

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

\[
\% D = \frac{C_{ads}}{C_{disp}} \times 100\%
\]

The regeneration efficiency was determined using the equation:

\[
\% \text{ regeneration} = \frac{Q_f}{Q_0} \times 100\% 
\]
The desorption of malachite green was tested by 50 mL of malachite green with a concentration of 100 mg/L before being added with 1 g 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 Na₂EDTA) 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.

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].

| Materials          | Sₘₐₓ (m²/g) | Pₑₓₑ (nm), BJH | Vₑₓₑ (cm³/g) |
|--------------------|-------------|----------------|--------------|
| Mg/Cr              | 21.511      | 3.20           | 6.564        |
| Mg/Cr-(COO)₂²⁻     | 49.270      | 0.158          | 6.511        |

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⁻.
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)$^{2-}$ 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)$^{2-}$ 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)$^{2-}$ had a greater interlayer distance than Mg/Cr LDH. BET analysis also showed that the Mg/Cr-(COO)$^{2-}$ 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)$^{2-}$ LDH adsorbent reached a shorter adsorption equilibrium after 30 minutes of adsorption process.

Table 2 shows that the adsorption of malachite green on Mg/Cr and Mg/Cr-(COO)$^{2-}$ as adsorbents followed the PSO kinetic model (based on R$^2$). The $k_2$ value of Mg/Cr-(COO)$^{2-}$ was smaller than that of Mg/Cr LDH. This indicated that the Mg/Cr LDH was slightly more reactive than the Mg/Cr-(COO)$^{2-}$. Malachite green adsorption with Mg/Cr LDH had $q_e$ of 57.126 mg/g while Mg/Cr-(COO)$^{2-}$ had $q_e$ of 68.124 mg/g. Thus, the results of the kinetic parameter for the Mg/Cr-(COO)$^{2-}$ 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 in the adsorption process. The adsorption of malachite green for Mg/Cr and Mg/Cr-(COO)$^{2-}$ LDH as adsorbents showed that the adsorption of dye on Mg/Cr-(COO)$^{2-}$ LDH was greater than that of Mg/Cr-LDH.

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 (R$^2$ >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 (Qmax) of malachite green adsorption for Mg/Cr and Mg/Cr-(COO)$^{2-}$ LDH obtained 33.784 mg/g (333K) and 64.516 mg/g (333K), respectively. The $q_e$ for Mg/Cr-(COO)$^{2-}$ 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 biochars had adsorption capacity of 30.18 mg/g [30]. Of all this study, the Mg/Cr-(COO)$^{2-}$ 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)$^{2-}$ LDH as adsorbents such as ∆H (enthalpy), ∆S (entropy), ∆G (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)$^{2-}$ LDH as adsorbents occurred spontaneously, as indicated by negative ∆G. The ∆H value in the range ∆H < -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 ∆S 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].

![Fig. 5. Time variation of adsorption malachite green onto Mg/Cr LDH and Mg/Cr-Oxalate LDH](image)

![Fig. 6. Concentration vs. malachite green uptake of Mg/Cr (a) and Mg/Cr-(COO)$^{2-}$ (b)](image)

**Table 2. Kinetic study malachite green removal**

| Adsorbent       | $Q_{theor}$ (mg/g) | $Q_{calc}$ (mg/g) | R$^2$  | $k_2$  | $Q_{calc}$ (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)$^{2-}$ | 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   |
| Langmuir            | Qmax                | 19.493              | 20.121| 30.864| 33.784|       |
| Mg/Cr               | k_L                 | 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 |       |
| Mg/Cr-              | k_F                 | 1.113               | 1.157 | 1.076 | 1.084 |       |
| Oxalate            | R^2                 | 0.999               | 0.993 | 0.999 | 0.965 |       |
|                     | Qmax                | 23.685              | 81.031| 64.053| 64.516|       |
| Mg/Cr-              | k_L                 | 0.001               | 0.002 | 0.035 | 0.062 |       |
| Oxalate            | R^2                 | 0.999               | 0.999 | 0.969 | 0.976 |       |
|                     | n                   | 0.029               | 0.140 | 0.140 | 0.871 |       |
|                     | k_F                 | 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_0 (mg/g) | ΔH (kJ/mol) | ΔS (kJ/mol) | ΔG (kJ/mol) |
|----------------------|-------|------------|-------------|-------------|-------------|
| 50                   | 303   | 26.556     | 7.976       | 0.028       | -0.398      |
| 313                  | 28.932|            |             |             |             |
| 323                  | 29.597|            |             |             |             |
| 333                  | 30.191|            |             |             |             |
| 303                  | 36.627| 4.591      | 0.019       | -1.096      |             |
| 313                  | 37.434|            |             |             |             |
| 323                  | 38.242|            |             |             |             |
| 333                  | 38.931|            |             |             |             |
| 303                  | 47.245| 2.530      | 0.014       | -1.729      |             |
| 313                  | 47.316|            |             |             |             |
| 323                  | 48.029|            |             |             |             |
| 333                  | 48.575|            |             |             |             |
| 303                  | 66.793| 9.202      | 0.039       | -2.747      |             |
| 313                  | 70.214|            |             |             |             |
| 323                  | 71.306|            |             |             |             |
| 333                  | 72.161|            |             |             |             |
| 303                  | 76.579| 5.955      | 0.030       | -3.043      |             |
| 313                  | 78.432|            |             |             |             |
| 323                  | 79.180|            |             |             |             |
| 333                  | 80.237|            |             |             |             |

The adsorption efficiency of malachite green using Mg/Cr and Mg/Cr-(COO)\textsuperscript{2}\ LDH adsorbents for the regeneration process was decreased. The amount of malachite green adsorption at first regeneration on Mg/Cr and Mg/Cr-(COO)\textsuperscript{2} 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)\textsuperscript{2} and was smaller in third regeneration process. The adsorption efficiency of the Mg/Cr-

Table 5. Thermodynamic parameter of adsorption malachite green onto Mg/Cr LDH

| Concentration (mg/L) | T (K) | Q_0 (mg/g) | ΔH (kJ/mol) | ΔS (kJ/mol) | ΔG (kJ/mol) |
|----------------------|-------|------------|-------------|-------------|-------------|
| 50                   | 303   | 27.055     | 27.991      | 0.094       | -0.481      |
| 313                  | 32.447|            |             |             |             |
| 323                  | 35.060|            |             |             |             |
| 333                  | 38.433|            |             |             |             |
| 303                  | 40.617| 19.642     | 0.071       | -1.796      |             |
| 313                  | 43.658|            |             |             |             |
| 323                  | 45.914|            |             |             |             |
| 333                  | 48.765|            |             |             |             |
| 303                  | 61.046| 22.796     | 0.091       | -4.640      |             |
| 313                  | 63.160|            |             |             |             |
| 323                  | 65.155|            |             |             |             |
| 333                  | 66.010|            |             |             |             |
| 303                  | 75.392| 15.436     | 0.065       | -4.113      |             |
| 313                  | 77.767|            |             |             |             |
| 323                  | 79.287|            |             |             |             |
| 333                  | 81.104|            |             |             |             |
| 303                  | 82.660| 19.730     | 0.078       | -3.878      |             |
| 313                  | 84.917|            |             |             |             |
| 323                  | 87.862|            |             |             |             |
| 333                  | 90.475|            |             |             |             |

Fig. 7. Desorption malachite green on Mg/Cr LDH and Mg/Cr-Oxalate LDH
(COO)\(^{2-}\) 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].

4. Conclusion

Mg/Cr LDH was successfully synthesized with (COO)\(^{2-}\) to form MgCr-(COO)\(^{2-}\) LDH was conducted by increasing the interlayer distance by 2.59 Å and surface area 49.270 m\(^2\)/g. Removal study of malachite green used Mg/Cr and MgCr-(COO)\(^{2-}\) 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 MgCr-(COO)\(^{2-}\) LDH to recycle after three times and effective to remove malachite green from wastewater.

Acknowledgements

Special thanks to Research Center of Inorganic Materials and Complexes, Faculty of Mathematics and Natural Science Universitas Sriwijaya for analysis and instrumental characterization. This research was supported by Hibah Disertasi Doktor with contract number 150/E4.1/AK.04/PT/2021 as additional output-based research.

References

1. M. Chincholi, P. Sagwekar, C. Nagaria, S.I. Kulkarni, S. Dhekpaunde, Removal of Dye by Adsorption on Various Adsorbents: A Review, International Journal Engineering Science and Technology. 3 (2014) 835-840.

2. J. Yimratanaabovorn, S. Nophkhotud, S. Dararat, Removal of Reactive Dyes from Wastewater by Shale, Sonlanakarin Journal of Science and Technology. 34 (2012) 117–123.

3. M.L. Firdaus, N. Krsinanto, W. Alwi, R. Muhammad, M.A. Serunting, Adsorption of Textile Dye by Activated Carbon Made from Rice Straw and Palm Oil Middiy, Ache International Journal of Science and Technology. 6 (2017) 1–7.

4. M.S.I. Mozumder, M.A. Islam, Development of Treatment Technology for Dye Containing Industrial Wastewater, Journal of Scientific Research. 2 (2010) 567.

5. J. Rahmadan, V. Parhuis, N.R. Palapa, T. Taher. R. Mohadi, A. Lesbani, ZnAl-Humic Acid Composite as Adsorbent of Cadmium (II) From Aqueous Solution, Science and Technology Indonesia. 6 (2021) 247-255.

6. D. Sun, Z. Zhang, M. Wang, Y. Wu, Adsorption of Reactive Dyes on Activated Carbon Developed from Enteromorpha prolifera, American Journal of Analytical Chemistry. 4 (2013) 17–26.

7. L.A. Mikif, N. Abdulhusin, H.M. Jail, J.M. Salman, Removal of Organic Matters from Domestic Wastewater by Using Adsorption Technique, Mesopotamia Environmental Journal. 4 (2018) 16–24.

8. N.R. Palapa, N. Juleanti, N. Normah, T. Taher, A. Lesbani, Unique Adsorption Properties of Malachite Green on Interlayer Space of Cu-Al and Cu-Al-SiW\(_6\)O\(_{34}\) Layered Double Hydroxides, Bulletin of Chemical Reaction Engineering & Catalysis. 15 (2020) 653–661.

9. P. Semeraro, P. Fini, M. D’Addabbo M, F. Rizzi, P. Cosma, Removal from Wastewater and Recycling of Azo Textile Dyes by Alginate-Chitosan Beads, International Journal of Environment Agriculture and Biotechnology. 2 (2017) 1835–1850.

10. A.S. Sartape, A.M. Mandhare, V.V. Jadhav, P.D. Raut, M.A. Anuse, S.S. Kolekar, Removal of Malachite Green Dye from Aqueous Solution with Adsorption Technique Using Limonia Acidissima (Wood apple) Shell as Low Cost Adsorbent, Arabian Journal of Chemistry. 10 (2017) S3229–S3238.

11. N.R. Palapa, T. Taher, A. Wijaya, A. Lesbani, Modification of Cu/Cr Layered Double Hydroxide In Keggin Type Polyoxometalate as Adsorbent of Malachite Green from Aqueous Solution. Science and Technology Indonesia. 6 (2021) 209-217.

12. S. Sivamani, G.B. Leena, Removal of Dyes from Wastewater using Adsorption-a Review, International Journal Biosciences Technology. 2 (2009) 47–51.

13. R. Shan, L. Yan, Y. Yang, K. Yang, S. Yu, H. Yu, B. Zhu, B. Du, Highly Efficient Removal of Three Red Dyes by Adsorption onto Mg-Al-Layered Double Hydroxide, Journal of Industrial and Engineering Chemistry. 21 (2015) 561–568.

14. V. Correcher, J.G. Guinea, Cathodo- and Photoluminescence Emission of a Natural Mg-Cr Carbonated Layered Double Hydroxide, Applied Clay Science. 161 (2018) 127–131.

15. S. Boutera, F.B.D. Saiah, S. Hamonda, N. Bettahar, Zn-M-Co\(_2\) Layered Double Hydroxides (M=Fe, Cr, or Al): Synthesis, Characterization, and Removal of Aqueous Indigo Carmine, Bulletin of Chemical Reaction Engineering & Catalysis. 15 (2020) 43–54.

16. T. Taher, Y. Irianty, R. Mohadi, M. Said, R. Andreas, A. Lesbani, Adsorption of Cadmium(II) Using CuAl Layered Double Hydroxides Intercalated with Keggin Ion, Indonesian Journal of Chemistry. 19 (2019) 873–881.

17. D. Giscard, T. Kamgang, R.C.T. Temgoua, E. Ymele, F.M.M. Tchieno, I.K. Tonlé, Intercalation of Oxalate Ions in The Interlayer Space of a Layered Double Hydroxide for Nickel Ions Adsorption, International Journal of Basic and Applied Sciences. 5 (2016) 144.

18. N.R. Palapa, R. Mohadi, A. Racmat, A. Lesbani, Adsorption Study of Malachite Green Removal from Aqueous Solution Using CuM\(_{10}^{+}\)\((M=\text{Al}, \text{Cr})\) Layered Double Hydroxide, Mediterranean Journal of Chemistry. 10 (2020) 33–45.

19. Y.S. Asci YS, Removal of Textile Dye Mixtures by Using Modified Mg-Al-CI Layered Double Hydroxide (LDH), Journal of Dispersion Science and Technology. 38 (2017) 923-929.

20. G. Darmograi, B. Prelot, G. Layrac, D. Tichit, G. Martin-Gassiot, Study of Adsorption and Intercalation of Orange-Type Dyes into Mg-Al Layered Double Hydroxide, The Journal of Physical Chemistry C. 119 (2015) 23388–23397.

21. S. Mandal, S. Tripathy, T. Paldi, M.K. Sahu, R.K. Patel, Removal Efficiency of Fluoride by Novel Mg-Cr Layered Double Hydroxide by Batch Process from Water, Journal of Environmental Sciences. 25 (2013) 993–1000.

22. M. Moller, A. Pich, Development of Modified Silicate with Superior Adsorption Properties for Uptake of Pollutants from Air and Water, Thesis, RWTH Aachen University, 2017.

23. N.R. Palapa, T. Taher, B.R. Rahayu, R. Mohadi, A. Racmat, A. Lesbani, CuAl LDH/Rice Husk Biochar Composite for Enhanced Adsorptive Removal of Cationic Dye from Aqueous Solution, Bulletin of Chemical Reaction Engineering & Catalysis. 15 (2020) 525–537.

24. A.S. Prakash, P.V. Kanath, M.S. Hegde, Synthesis and Characterization of The Layered Double Hydroxides of Mg with Cr. Materials Research Bulletin. 35 (2000) 2189–2197.

25. P. Saikia, A. Gautam, R.L. Goswamee, Synthesis of Nanohybrid Alkogels of SiO\(_x\) and Ni-Cr/Mg-Cr-LDH: Study of Their Rheological and Dip Coating Properties, RSC Adv. 6 (2016) 112092–112102.
26. M. Arco, S. Gutie, C. Marti, V. Rives, Intercalation of [Cr(C₂O₄)₃]³⁻ Complex in MgAl Layered Double Hydroxides, Inorganic Chemistry. 42 (2003) 4232–4240.

27. H.K. Chung, W.H. Kim, J. Park, J. Cho, T.Y. Jeong, P.K. Park, Application of Langmuir and Freundlich Isotherms to Predict Adsorbate Removal Efficiency or Required Amount of Adsorbent, Journal of Industrial and Engineering Chemistry. 28 (2015) 241–246.

28. A.O. Dada, A.P. Olalekan, A.M. Olatunya, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn²⁺ Unto Phosphoric Acid Modified Rice Husk, IOSR Journal of Applied Chemistry. 3 (2012) 38–45.

29. S. Bahri, M. Muhdarina, N. Nurhayati, F. Andiyani, Isoterma dan Termodinamika Adsorpsi Kation Cu²⁺ Fasa Berair pada Lempung Cengar Terpilat, Jurnal Natur Indonesia. 14 (2012) 7-13.