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Research Article

Size Selectivity of Anionic and Cationic Dyes Using LDH Modified Adsorbent with Low-Cost Rambutan Peel to Hydrochar

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Abstract

Modification of the layered double hydroxide of CuAl-LDHs by composite with hydrochar (HC) to form CuAl-HC LDH. Material characterization by XRD, FT-IR and SEM analysis was used to prove the success of the modification. The characterization of XRD and FT-IR spectra showed similarities to pure LDH and HC. Selectivity experiments were carried out by mixing malachite green, methylene blue, rhodamine-B, methyl orange, and methyl red to produce the most suitable methyl blue dye for CuAl-LDH, HC and CuAl-HC adsorbents. The effectiveness of CuAl-HC LDH as adsorbent on methylene blue adsorption was tested through several influences such as adsorption isotherm, thermodynamics, and adsorbent regeneration. CuAl-HC LDH adsorption isotherm data shows that the adsorption process tends to follow the Langmuir isotherm model with a maximum adsorption capacity of 175.439 mg/g with a threefold increase compared to pure LDH. The effectiveness of the adsorbent for repeated use reaches five cycles as evidenced by the maximum capacity regeneration data reaching 82.2%, 79.3%, 77.9%, 76.1%, and 75.8%.

Keywords: CuAl-LDHs; Hydrochar; Composite; Selectivity; Regeneration

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1. Introduction

Industrial development is increasing to meet market needs and the needs of the mass population, so industrial waste is also increasing which can cause environmental pollution [1,2]. Based on many studies, researchers report that it is estimated that more than 7×10^5 tons of substances approximately 12–14% of the color produced annually become industrial waste after the manufacturing process and disposal in the environment [1,3,4]. Industrial sources that use

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a lot of dyes usually come from several industries such as paper, plastics, cosmetics, photography, food, ink, refining, pharmaceutical and textile industries [5–8]. In general, dyes are classified as cationic dyes and anionic dyes [1]. Methylene blue (MB) with the chemical formula $C_{16}H_{18}ClN_3S$ is one of the most abundant cationic dyes and is most commonly applied in industrial, biological, and chemical dyes [4,5,9]. Dyes usually have a stable aromatic complex structure so that the warning substance will be more difficult to decompose/degrade in nature [7]. However, its disposal directly into the environment will have a negative effect on both aquatic life and humans. This is because dyes are mutagenic, carcinogenic, and toxic/poisonous [2]. Water contamination by various organics discharged from industry into the environment has recently become dyes [10]. Thus, this issue should be addressed to remove and decontaminate dyes from wastewater to ensure a safe environment using efficient water treatment technologies [8,9].

Currently, many researchers report that there are several methods that have been developed to remove pollutants in wastewater. In general, various methods, physics and biology are used in wastewater treatment, such as electrochemistry, oxidation, biodegradation, chemical chemistry, coagulation, photocatalysis, membrane filtration, flocculation, ion exchange, ozonation, filtration, and adsorption [4,6,11,12]. Among these methods, adsorption is the most appropriate method and has many advantages for removing methylene blue from wastewater. This adsorption method has many advantages such as having high efficiency, easy to carry out, cost-effective alternative, simple method, easy to operate, produces unwanted by-products, and availability of large amount of adsorbent [13–16]. On the other hand, the important factor that has the greatest influence on the adsorption efficiency is represented by the adsorbent [17]. The effectiveness of the adsorbent in the adsorption process is one of the factors to obtain high adsorption capacity, large selectivity, thermal and chemical, and easy preparation [17,18]. Many adsorbents have been applied to remove methylene blue from solution, such as kaolin, activated carbon, cellulose, coal fly ash, bentonite, biomass, chitosan, as well as layered double hydroxide [3,7,16,19–21].

Recently developed materials have been developed. One of them is a layered material whose synthesis is layered double hydroxide (LDH) which has an adjustable usage density and great chemical uniformity [18]. LDH is an anionic clay with a positively charged layer [22,23]. This structure greatly contributes to its anionic exchange capacity. LDH or materials such as hydrotalcite have a chemical composition expressed by the formula $[M^{2+}1\text{-}xM^{3+}x(OH)_2]^{x+}$ $[A^{n-}{}_{x/n}.mH_2O]$ with metal substitution M^{3+} for M^{2+}, and an anion-containing interlayer and molecular solvation, where $M^{2+}$is like; Mg^{2+}, Zn^{2+}, or Ni^{2+}, and M^{3+}, such as; Al^{3+}, Ga^{3+}, Fe^{3+}, or Mn^{3+}. The A^{n-} is the anion present in the layer, *i.e.* CO_3, Cl^-, SO_4, RCO_2, while *x* are typically between 0.2 and 0.4 [13,24–26]. LDH has been widely used as a dye adsorbent because it has a high adsorption capacity and has a large surface area [14].

On the other hand, repeated use of LDH is ineffective because the structure of LDH will be exfoliated [27]. Therefore, it is necessary to improve the structure of LDH by modifying LDH. One of them, LDH modification can be done by forming a composite that combines two materials [28]. One of the materials that can be composited with LDH is a carbon-based material. Based on research by Lesbani *et al*. [14], NiAl LDH composited with biochar and used to adsorb methylene blue (MB). Biochar from rice husk was used as a matrix for the formation of NiAl LDH/Biochar composites. This adsorbent has an adsorption capacity of 61.72 mg/g, while pure LDH only reaches 22.98 mg/g. In a recent study conducted by Kundu & Naskar, (2021) [15] modification of LDH with carbon into carbon-LDH nanocomposite was applied to remove inorganic contaminants (metals of As(V), Fe(II)/Fe(III), F^-) and organic (methylene blue and methyl orange) in aqueous solution.

This study modified CuAl-LDH by forming a composite with hydrochar from rambutan peel (*Nephelium lappaceum L.)* which was applied as an adsorbent to remove methylene blue. This study used the coprecipitation method for the synthesis of CuAl-LDH. CuAl-LDH is made of divalent and trivalent metals, namely divalent Cu^{2+} metal cations and trivalent Al^{3+} metal cations. Divalent copper(II) metal was chosen in the LDH synthesis because it has advantages compared to other metals such as low resistance, active sites derived from Cu^{2+} metal and copper ion dispersion which will result in good adsorption performance. Furthermore, CuAl-LDH was composited with hydrochar from rambutan peel (*Nephelium lappaceum L*). The synthesized materials were characterized using XRD, FT-IR, and SEM analysis. The material will be applied as an adsorbent by influencing the adsorption selectivity of mixed dyes,

adsorption isotherms, adsorption thermodynamics and regeneration studies of each adsorbent.

2. Materials and Methods

2.1 Materials

The reagents used for the manufacture of CuAl-LDHs are copper(II) nitrate ($Cu(NO_3)_2{\cdot}3H_2O$, MW= 241.60 g/mol, purity ≥98%) by LOBA Chemie, aluminum(III) nitrate, ($Al(NO_3)_3.9H_2O$, MW= 375.13 g/mol, purity ≥98%) by Sigma Aldrich, iron(II) chloride ($FeCl_2.4H_2O$, MW= 198.83 g/mol, purity ≥99%) by Merck , hydrochloric acid (HCl, MW= 36.458 g/mol, 37%), sodium hydroxide (NaOH, MW= 40.00 g/mol by Merck, and the basic ingredient of hydrochar is rambutan peel.

2.2 Methods

2.2.1 Hydrothermal carbonization

Hydrothermal carbonization [29] experiments were carried out using 2.5 g of rambutan peel (*Nephelium lappaceum* L.) then added with 50 mL of distilled water which was put into a stainless steel autoclave hydrothermal device and sealed. The autoclave has a high pressure heating system according to the literature of Akarsu *et al.* [30]. The autoclave reaches a temperature of 200 ℃ for 10 hours. At the end of the process, the autoclave tool is at room temperature and the product in the autoclave is filtered to separate the filtrate and residue through filter paper. The solid (hydrochar/HC) was dried at 105 ℃ for 24 hours. the mechanism preparation of hydrothermal carbonization was shown in Figure 1.

2.2.2 Synthesis CuAl-LDHs

CuAl-LDH was synthesized using the coprecipitation method [27] by mixing 100 mL (0.75 M) copper(II) nitrate with 100 mL aluminum(II) nitrate (0.25 M). The mixture was stirred and 1 M NaOH solution was added dropwise until the mixture reached pH 10. The mixture was heated at 80 ℃ and maintained for 20 hours. The final process is carried out by separating the product using a vacuum, then the filtrate is dried at a temperature of 50 ℃ to dry.

2.2.3 Preparation modified CuAl-LDH

The modification of CuAl-LDHs into CuAl-HC LDH composites was prepared using the coprecipitation method, namely precipitation using an alkaline solution (KOH or NaOH). The preparation process was made with 30 mL (0.75 M) copper(II) nitrate with 30 mL (0.25 M) aluminum(III) nitrate mixed and stirred and kept for 1 hour until a gel was formed. The CuAl-LDHs gel mixture was added by slowly dripping 2 M NaOH solution until it reached pH 10. The gel mixture was added with 3 g of hydrochar from rambutan peel then the solution was stirred and kept at 80 °C for 3 days. The product from the preparation process was filtered to obtain a precipitate, the precipitate was rinsed with distilled water, and the resulting product was dried at 50 °C for 24 hours.

2.2.4 Adsorption experiment

The first experiment was to parameterize the adsorption selectivity of a mixture of several dyes, namely malachite green (MG), methylene blue (MB), rhodamine-B (Rh-B), methyl orange (MO), and methyl red (MR). The dye selectivity process is carried out by mixing 100 mL of each dye with the same concentration (10 mg/L) which is put into a 500 mL beaker, then the dye mixture is homogenized and after being homogeneous, take 50 mL of the solution. The mixture was put into a beaker and added as much as 0.05 g of adsorbent. The beaker containing the adsorbent and solution was then placed on a shaker to carry out the adsorption selectivity process by varying the adsorption contact time from 0, 15, 30, 60 to 120 minutes. the final process after the adsorption process, the mixture was separated by a centrifugation process to obtain the filtrate and residue, then the filtrate was analyzed using a UV-Vis spectrophotometer to scan the wavelength of the dye mixture solution.

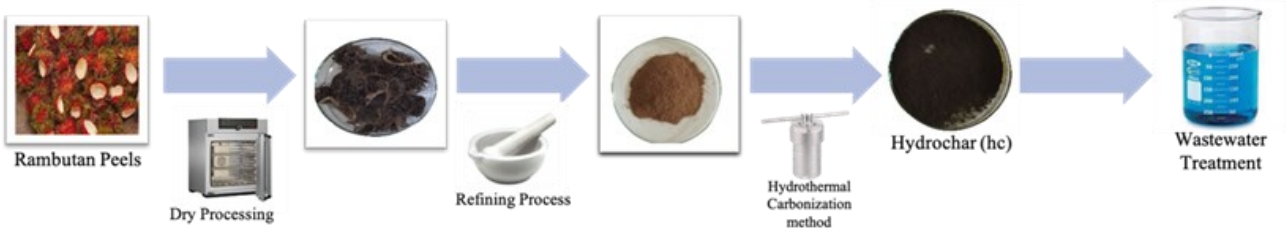

Figure 1. Mechanism of preparation and application of materials

The second experiment, isotherm and thermodynamic parameters by influencing variations in the initial concentration of dye by varying the temperature in the adsorption process with the following treatment in this study using variations in dye concentration (60, 70, 80, 90 and 100 mg/L), taken 20 mL was put into a beaker and 0.02 g of adsorbent was added, then the temperature was varied (303, 313, 323, and 333 K). The mixture was stirred for 2 hours and maintained at various temperatures used during the adsorption process.

The third experiment is the study of regeneration. But before the regeneration process must be carried out the desorption process first. In this study, 50 mL of methylene blue solution (50 mg/L) was put into a beaker and added 0.5 g of adsorbent, then stirred for 2 hours using a shaker. Then, when finished, separate the filtrate and residue. The absorbance value of the filtrate was measured using a UV-Vis Spectrophotometer and dried the residue remaining from the adsorption process at 40 °C. After the adsorbent is dry, take 0.01 g and add it to a solution of 10 mL of water that has been put in a beaker and place it on an ultrasonic device for 2 hours for the desorption process, separate the filtrate and residue, then dry the residue at 40 °C. Then, The regeneration process was carried out using a dry adsorbent that had gone through the desorption process, 50 mL of methylene blue solution (100 mg/L) was added to the dry adsorbent and stirred for 2 hours. The mixture was separated between residue and filtrate, the filtrate was taken and measured using a UV-Vis spectrophotometer, while the residue from the separation was dried and then used for the desorption process again with water. The dry adsorbent that has gone through the desorption process is then reused for the regeneration process. The process was carried out for seven cycles with the same treatment.

2.2.5 Characterization

CuAl-LDHs, HC, and CuAl-HC composites were characterized by FT-IR spectroscopy (Shimadzu FT-IR Prestige-21). The morphology of the material was determined by SEM characterization. The powder material was characterized by XRD using a diffactometer (Rigaku Miniflex-600) with monochromatic radiation of Cu-Kα in the range (2θ) 5-60° with a scanning speed of 2°/min. MB was analyzed using UV-Visible Spectrophotometer (Biobase BK-UV 1800 PC), and measured at a maximum absorbance wavelength of about 664 nm.

3. Results and Discussion

First, XRD technique was used to confirm the crystallographic structure of CuAl-LDHs, HC and composites modified by CuAl-LDHs with hydrochar (HC) obtained after using the coprecipitation method. As shown in Figure 2, Diffractograms of CuAl-LDH, HC and CuAl-HC composites are seen with sharp Bragg reflections and peaks observed at an angle of 2θ ranging from 5–80° For CuAl-LDHs, it has sharp peaks at an angle of 2θ = 11.72°, 23.51° and 35.59°, which can be attributed to the crystal planes of (003), (006) and (009) of pure CuAl-LDHs according to JCPDS No.36-0630 [31]. According to Szabados *et al.* [32] reflections at (012) indicate compounds $M^{2+}(OH)_2$ and $M^{3+}(OH)_3$, where (009) indicates byproduct

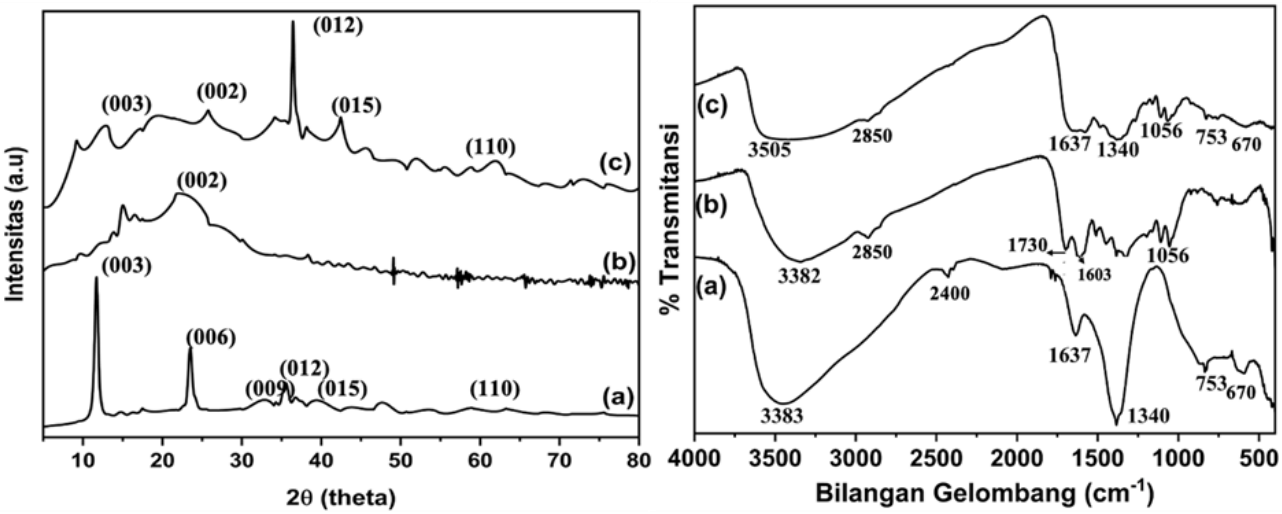

Figure 2. X-ray Powder diffraction patterns and spectrum FT-IR of CuAl-LDHs (a) HC(b) and Composite CuAl-HC(c).

compounds in LDHs, such as carbonate anions, nitrates, present in the interlayer or mixtures of metal oxides that cause peaks in the LDHs reflection (009) amorphous. This phenomenon indicates that a layered double hydroxide layered structure was successfully formed. According to Palapa *et al*. [27], the characteristic of the CuAl-LDHs diffraction pattern that appears has high crystallinity and the formation of hydrotalcite. The modified CuAl-HC composite was seen to have a decreased intensity and a widening peak indicating that the crystallinity was decreased. This is triggered by the modification of LDH with HC, where HC has amorphous characteristics shown at an angle of 2θ, which is 22° (002) [33]. In addition, CuAl-HC showed an XRD pattern similar to pure CuAl-LDHs, this proves that the modified treatment by composited LDH with HC did not change the layer structure of LDH.

The FTIR is spectrum shown in Figure 2. is the spectrum of CuAl-LDHs, HC, and CuAl/HC materials. It can be seen in the figure that CuAl-LDH has a peak width of about 3382 cm^{-1} which is related to the OH vibration of the hydrogen bonded metal on the surface of the layer, the peak around 2400 cm^{-1} is related to the vibration of CO_2 gas present during the synthesis and 1637 cm^{-1} shows the vibration H–OH water molecules present in the interlayer [13], 1340 cm^{-1} associated with the nitrate anion present in the interlayer (NO_3 ion), the vibration at the peak of about 753 cm^{-1} and 670 cm^{-1} associated with oxygen-bound metal in the framework of LDHs (Cu–O, Al–O, Cu–O–Cu, Al–O–Al, O–Cu–O and O–Al–O). The peak is around 500 cm^{-1} which indicates the presence of metal hydroxides in the LDH layer [34]. Figure 2 shows that the spectrum of hydrochar has a peak of about 3383 cm^{-1} associated with the vibration of water molecules and a peak around 2850 cm^{-1} indicating the aliphatic C–H group vibration, the vibration peak of around 1730 cm^{-1} and 1607 cm^{-1} associated with the vibration of the C=O group, and 1056 cm^{-1} associated with the vibration of the C=C group. The modified material, namely the CuAl-HC composite, has a vibration similar to that of pure LDH and HC. The presence of these various vibrational peaks confirms the successful modification of LDH with HC.

Figure 3 analyzes the material prepared from CuAl-LDHs, HC and modified pure LDH with HC to CuAl-HC using an SEM that aims to see the surface morphology of the material obtained through scanning electron microscopy (SEM). The encapsulated powder is shown in Figure 3. Figure 3(a) shows that the LDH adsorbent has a rough, uneven surface texture and irregular pores. In contrast to the HC shown in Figure 3(b), the surface morphology of the HC prepared using the hydrothermal carbonization (HTC) method looks shaped like balls measuring (1–10 μm). Figure 3(c) shows the morphology of the CuAl-HC composite material which shows an uneven and rough surface.

The selectivity of dyes on each adsorbent CuAl-LDHs, HC, and CuAl-HC was carried out by measuring the maximum wavelength of a mixture of dye solutions of MG, MB, Rh-B, MR,

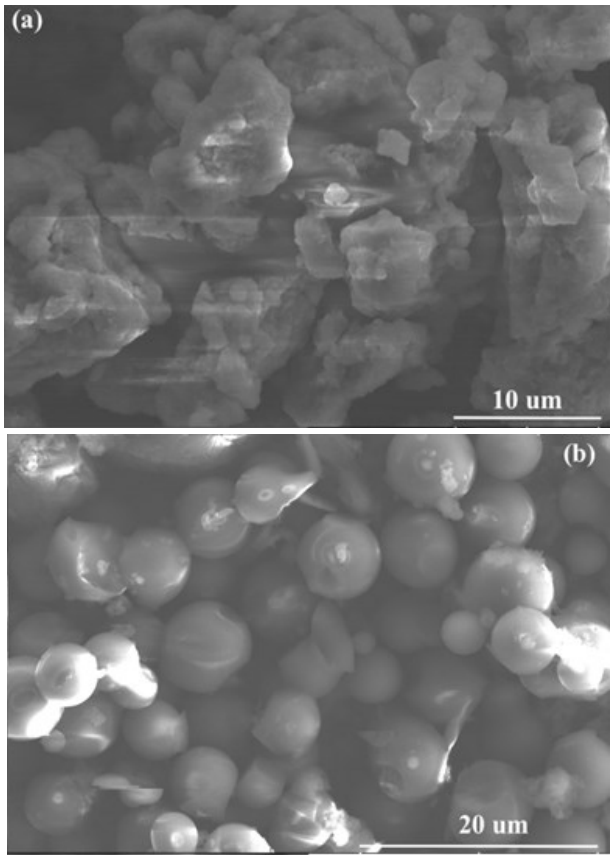

Figure 3. SEM image of CuAl-LDHs (a) HC(b) and Composite CuAl-HC(c).

CR and MO without the influence of pH using a UV-UV spectrophotometer. Vis in the wavelength range between 400–700 nm. The results of the measurement of the wavelength at the maximum absorbance are shown in Figure 4. The selectivity of adsorption on the dye mixture can be seen from the change in the wavelength of the maximum absorbance during the adsorption process according to variations in time. Figure 4 shows that the absorbance of CuAl-LDHs, HC and CuAl-HC adsorbents decreased with increasing adsorption contact time. Among these dye mixtures, MB dye was seen for CuAl-LDHs, HC, and CuAl-HC adsorbents more adsorbed than MG, Rh-B, MR, CR and MO. A drastic decrease in absorbance value oc-

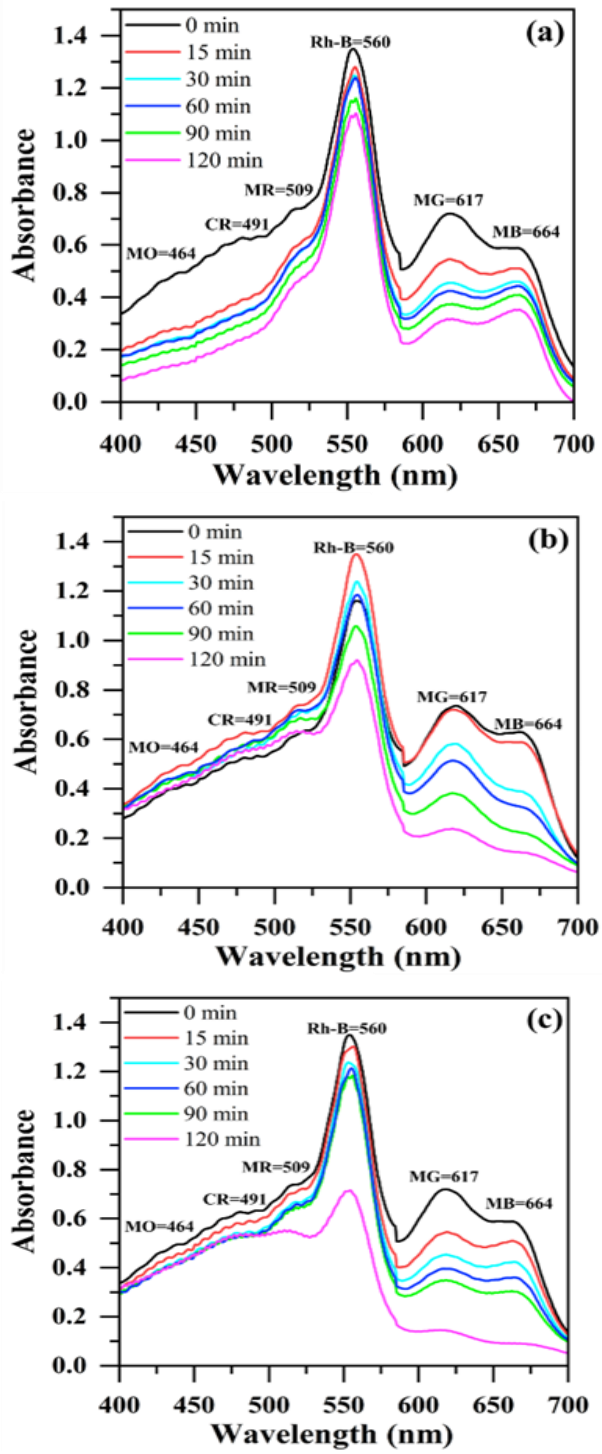

Figure 4. UV-Visible spectra of mixture MB, MG, Rh-B, MR, CR, and MO on CuAl-LDHs (a), HC (b), and CuAl-HC (c).

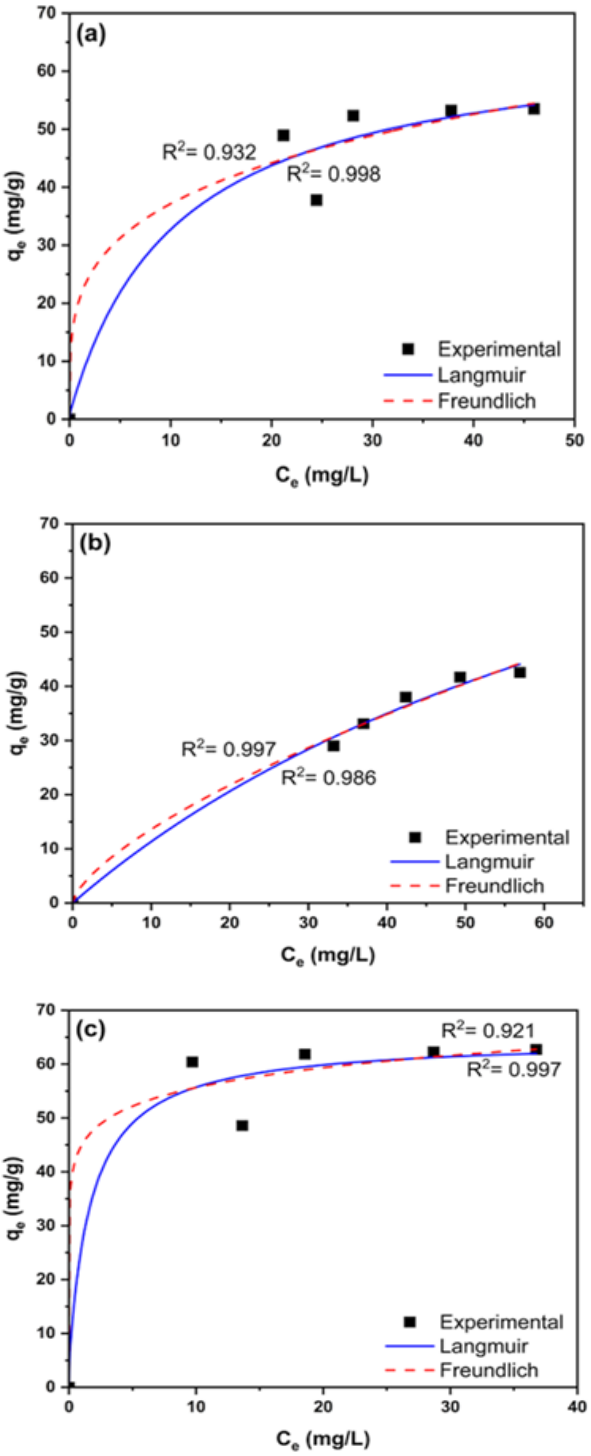

Figure 5. Adsorption isotherm model of MB using CuAl-LDHs (a), HC (b), and CuAl-HC (c).

curred at 120 minutes with the adsorbed reaching 9.465 mg/g for CuAl-HC adsorbent, while CuAl-LDHs and HC reached 3.876 mg/g and 8.234 mg/g, respectively. After knowing the most selective MB dye, the MB dye continued to the isotherm adsorption and thermodynamic adsorption process which looks like Figure 5.

Adsorption study with adsorption isotherm treatment was carried out by varying the initial concentration of MB by varying the adsorption temperature. Determining the Langmuir and Freundlich adsorption isotherm model determined according to the equation based on the literature [22,35]. The isotherm parameters are obtained from the Langmuir and Freundlich equations. Langmuir and Freundlich isotherm equations are as follows:

$$\text{Langmuir} \quad : \quad \frac{C}{m} = \frac{1}{bK_{ML}} + \frac{C}{b} \tag{1}$$

$$\text{Freundlich} \quad : \quad \log q_e = \log K_F + \frac{1}{n}\log C_e \tag{2}$$

where C is a saturated concentration of adsorbate, m is the amount of adsorbate, b is the maximum adsorption capacity ($mg.g^{-1}$), K_{ML} is the Langmuir constant ($L.mg^{-1}$), q_e is adsorption capacity at equilibrium ($mg.g^{-1}$), C_e is a concentration of adsorbate at equilibrium ($mg.L^{-1}$), K_F is Freundlich constant.

Determination of the isotherm model of an adsorption process can be determined based on the linear regression value R^2>0.932 (which is close to 1). Figure 5 shows the profile of the Langmuir and Freundlich isotherm model. Figure 5 shows that Figure 5(a) is CuAl LDH and 5(b) is HC, each of which has a smaller adsorption capacity (q_e (mg/g) compared to Figure 5(c) which is a CuAl-HC composite that has a larger adsorption capacity so that it can be seen from the curve of Figure 5 CuAl LDH and HC look lower. It can be seen that MB adsorbed with CuAl-LDH, HC and CuAl-HC tends to have a R^2 value closer to 1, namely the Langmuir isotherm model. This is supported by the calculated data presented in Table 1.

From Table 1 it can be seen that the Langmuir Isotherm calculates the Langmuir constant (k_L), and shows the suitability of the model for the adsorption system. If the k_L value is between 0 and 1, the system is considered suitable for adsorption [36] and Table 1 shows the results which are in the range of 0.293; 0.080; 0.074. Furthermore, the adsorption isotherm data is also equipped with the Freundlich equation with parameters k_F and n which indicate the preference of the adsorbent/adsorbate system, where the value of k_F is a constant for the system, which is related to the binding energy [5] and the adsorption capacity of Freundlich (k_F) according to with data obtained respectively 19.843; 4.870; 0.920 for CuAl-LDH, HC and CuAl-HC, while the adsorption intensity represented by the value of n indicates the suitability of the adsorption isotherm model for adsorption if the value of n is above 1. From Table 1 it can be seen that the value of n CuAl-LDH, HC and CuAl- HC each of 3.792; 4.651; 10.560.

According to the literature Araújo *et al.* [12], the adsorption process with a tendency to follow the Langmuir isotherm model shows that the adsorption that occurs is the formation of a monolayer and the weak force or interaction between the adsorbent and the adsorbate is the result of physical interaction. The Langmuir model is based on the assumption that it has the same active site so that the surface is homogeneous and the coverage of monolayer formation is without interactions between the adsorbed molecules [37]. In addition to determining the adsorption isotherm model, the data in Table 1 presents the maximum capacity. The use of different adsorbents for MB dye causes different adsorption capacities in each process according to the capacity or ability of the adsorbent. MB adsorption process using modified adsorbent, namely CuAl-HC composite has a maximum adsorption capacity of 175.439 mg/g while pure LDH material reaches 57.803 mg/g. The modified capacity had the adsorption capacity which increased drastically by increasing threefold from the pure LDH.

The comparison of MB absorption for several adsorbents is presented in Table 2. Table 2 shows that the adsorption capacity of several adsorbents for MB dye and the comparison using the prepared adsorbents in the form of

Table 1. Isotherm model of MB adsorption on CuAl-LDHs,HC and CuAl-HC.

Materials	Langmuir		Freundlich	
	q_m (mg/g)	k_L	n	k_F
CuAl LDH	57.803	0.293	3.792	19.843
HC	49.286	0.080	4.651	4.870
CuAl LDH-HC	175.439	0.074	10.560	0.921

CuAl-LDHs, HC and CuAl-HC in the study. MB adsorption capacity for CuAl-LDHs, HC and CuAl-HC adsorbents has a greater adsorption capacity than other adsorbents and it can be seen that the modified CuAl-LDH material has a greater adsorption capacity for MB adsorption.

Thermodynamic parameters related to the change in Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) can be calculated using the Van't Hoff equation as follows [42].

$$\Delta G = -RT \ln K_d \quad (3)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

K_d is the solute distribution coefficient (L/g), R is the universal gas constant (8.314 mol/K), T is temperature (K), Gibbs free energy (ΔG°, kJ/mol), entropy (ΔS°, kJ/mol), and enthalpy (ΔH°, J/mol.K).

The plot of ln K_d vs 1/T, is shown in Figure 6. The thermodynamic parameter values obtained from the slope and intercept of the van't Hoff plot are shown in Table 3. The appropriate van't Hoff plot is used to calculate

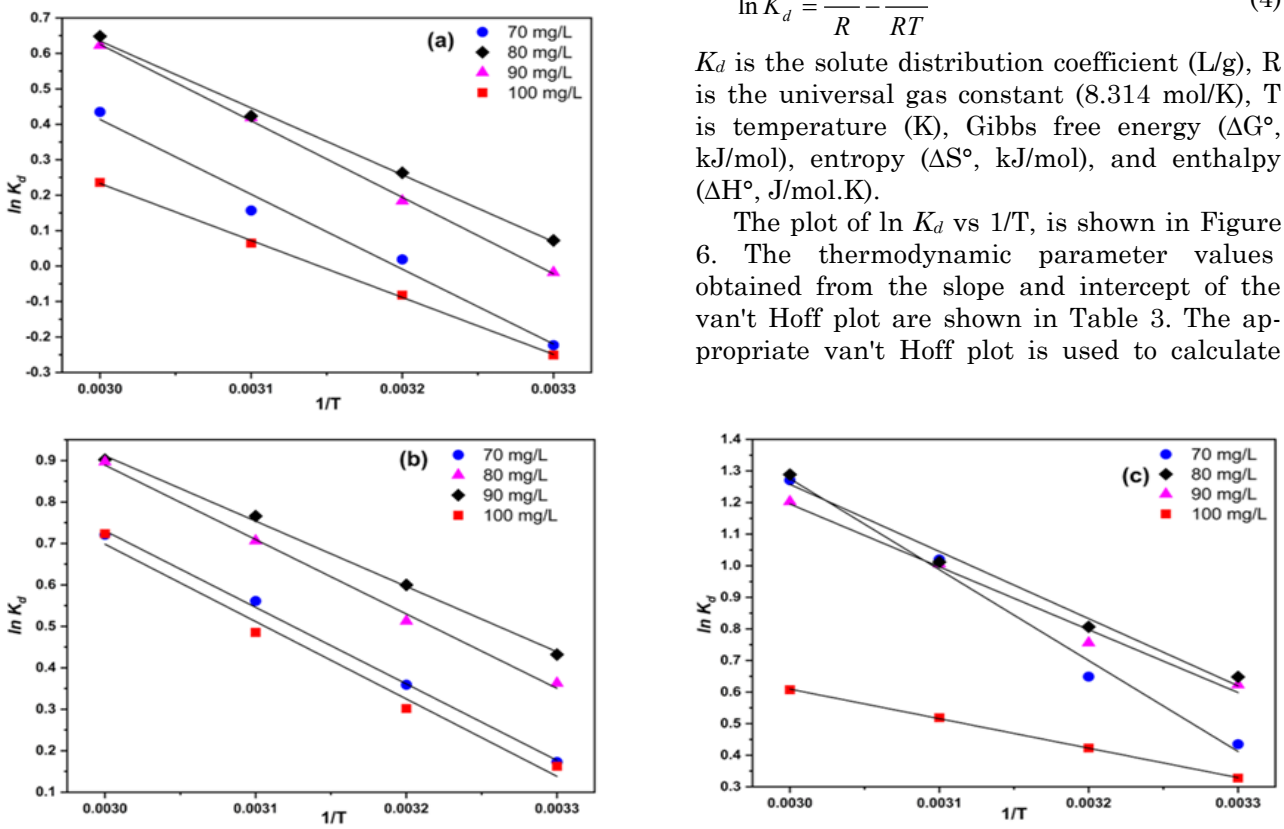

Figure 6. Van't Hoff plot for adsorption of MB on CuAl-LDHs (a), HC (b), and CuAl-HC (c).

Table 2. Comparison of several adsorbents to removal MB.

Adsorbent	Adsorption Capacity (mg/g)	Reference
3D-MgAl-LDH	54.3	[38]
$NiFeTi_2$-LDH	29.940	[39]
Zn-Fe LDH	32.894	[40]
Mn-Fe LDH	43.103	[40]
Activated Carbon from Coconut Shell	15.423	[19]
Activated Carbon developed from *Ficus carica* bast	47.62	[41]
Organo/ZnAl-LDH Nanocomposite	113	[13]
CuAl-LDHs	57.803	In this study
HC	49.286	In this study
CuAl-HC	175.439	In this study

Table 3. Thermodynamic parameters of MB adsorption on CuAl-LDHs, HC and CuAl-HC.

Parameters	T (K)	Materials		
		CuAl LDH	HC	CuAl LDH-HC
ΔG°	303	−0.343	−0.430	−0.368
	313	−0.980	−0.956	−0.739
	323	−1.617	−1.481	−1.109
	333	−2.254	−2.007	−1.479
ΔS°		0.064	0.053	0.037
ΔH°		18.963	15.503	10.851

the thermodynamic parameters using the slope and intercept equations van't Hoff [43] to determine the thermodynamic properties of adsorption.

The thermodynamic parameters yielded the data shown in Table 3. Data ΔH° (enthalpy), ΔS° (entropy), ΔG° (Gibbs free energy) were obtained from the equation according to the literature [44]. Table 3 shows the results with negative values for ΔG° in all adsorption temperature ranges used. ΔG° increased with adsorption temperature. Increasing the ΔG° value with increasing adsorption temperature, the ΔG° values are in the range of −0.343 kJ/mol to −2.254 kJ/mol (CuAl LDH), −0.430 kJ/mol to −2.007 kJ/mol (HC), and −0.368 kJ/mol to −1.479 kJ/mol (CuAl-HC), this indicates that there is a tendency to decrease the degree of adsorption feasibility of MB [45]. A negative value at ΔG° indicates that the adsorption process is spontaneous [46,47]. According to Batool *et al*. [48], the value of ΔG° decreases with increasing temperature. Reflecting that the adsorption that occurs is better at high temperatures. If the value of ΔH° has a range of −20 to 40 kJ/mol then the adsorption tends to be physical adsorption and in the range of 80 to 400 kJ/mol then the adsorption tends to be chemical adsorption. In this study, the ΔH° value showed a range of 10.851 kJ/mol to 18.963 kJ/mol with a physical adsorption tendency [49,50]. ΔH° is positive, this indicates that MB adsorption is endothermic and positive for S° with a value of 0.064 J/mol.K to 0.037 J/mol.K because the randomness during the adsorption process increases due to the solid-liquid interaction that occurs in the adsorption [51].

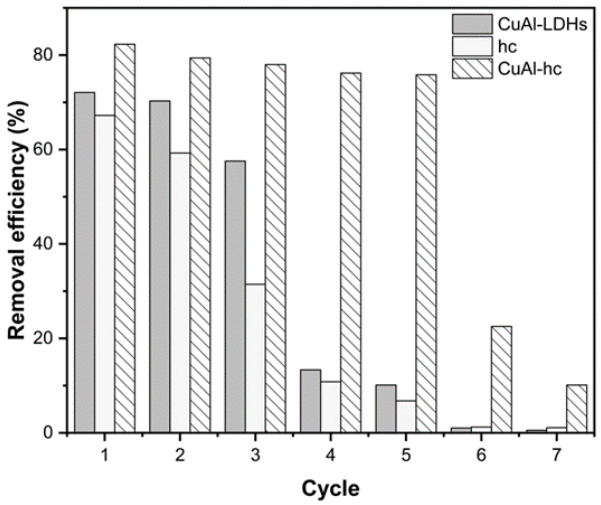

Figure 7. CuAl-LDHs, HC and CuAl-HC adsorbent regeneration ability.

The ability of the adsorbent to overcome contamination was also tested for the effectiveness of the ability of the adsorbent for the regeneration process in reuse. The regeneration process of CuAl-LDHs, HC, and CuAl-HC adsorbents was carried out for 7 repetition cycles, which is presented in Figure 7.

The test results for the regeneration process of CuAl-LDH, HC and CuAl-HC adsorbents to overcome dye pollution are presented in Figure 7. The results show that the modified CuAl-LDH material has advantages over pure LDH, this is evidenced by the higher adsorption capacity, stability for the adsorbent reuse process and has more absorption capacity which is supported by the active group factor possessed by the CuAl-HC composite material which is supported by the FT-IR characterization, where the CuAl-HC composite has more functional groups due to the combination of functional groups of pure CuAl LDH and HC materials. MB adsorption using CuAl-LDH modified material is stable for five regeneration cycles, this is due to the process of modifying LDH with composites or combining two materials such as LDH with hydrochar which can increase the active site of the material and structural stability because there is the protection of the LDH layer from hydrochar so that there is no peeling LDH layer and structural damage [35]. The CuAl-HC composite has an adsorption capacity of 82.2%; 79.3%; 77.9%; 76.1%; 75.8%, while CuAl LDH had an unstable adsorption capacity of 72.09% and decreased to 10.12%, HC had an adsorption capacity of 67.23% and decreased to 6.76%. So it can be concluded that the modification of LDH with hydrochar has a good regeneration ability.

4. Conclusion

Based on the data characterization of CuAl-LDH modified layered double hydroxide with composite with hydrochar (HC) to form LDH CuAl-HC by XRD, FT-IR and SEM analysis, the material was successfully produced which was shown by the appearance of peaks and vibrations similar to pure LDH and HC. CuAl-HC LDH was applied as adsorbent for methylene blue adsorption. CuAl-HC LDH adsorption isotherm data showed that the adsorption process tended to follow the Langmuir isotherm model (R^2>0.932) with a maximum adsorption capacity of 175.439 mg/g, an increase of three times from pure LDH with a maximum adsorption capacity of 57.803 mg/g. The data from thermodynamic parameters showed that the adsorption was spontaneous and endother-

mic. The effectiveness of the adsorbent for repeated use reaches five cycles as evidenced by the regeneration data and adsorption capacity of 82.2%, 79.3%, 77.9%, 76.1%, and 75.8%.

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