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Research Paper

Mg/Al-chitosan as a Selective Adsorbent in The Removal of Methylene Blue from Aqueous Solutions

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Abstract
The use of dyes in the textile industry is detrimental to aquatic biota and humans. Pollution caused by dye waste can be overcome by adsorption methods using adsorbents such as LDH. LDH is known as an adsorbent that is often found in the process of removing dye waste, but repeated use is not effective. This can be overcome by the LDH modification process using a supporting material such as chitosan. Modification of LDH can be done using coprecipitation or precipitation simultaneously at pH 10. XRD analysis where the peaks that appear in Mg/Al-chitosan are similar to the typical peaks of the constituent materials, namely Mg/Al and chitosan. This is confirmed by FTIR analysis where the spectrum that appears in Mg/Al-chitosan is similar to the spectrum in Mg/Al and chitosan. As well as BET analysis where there is an increase in the surface area of Mg/Al after being modified to Mg/Al-chitosan from 5.845 m^2/g to 24.556 m^2/g. In this study, the selectivity process for the dye mixture was carried out first with the most selective dye for the Mg/Al-chitosan adsorbent was methylene blue. Methylene blue was continued for adsorption processes such as isotherm adsorption kinetics and adsorption thermodynamics as well as adsorbent regeneration studies. The results showed that at 90 minutes the adsorption reached equilibrium. The adsorption capacity of Mg/Al increased after modification using chitosan from 84.746 mg/g to 108.696 mg/g. The adsorption process follows the Langmuir isotherm type where adsorption occurs chemically (monolayer). Regeneration studies show that Mg/Al-chitosan is an adsorbent that can be used repeatedly with stable adsorption effectiveness until the fifth cycle.

Keywords
Adsorption, Selectivity, Methylene Blue, Regeneration

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1. INTRODUCTION

The increasing use of dyes in various industries such as food and textiles can cause serious environmental problems. Disposal of large volumes of waste into the environment causes adverse effects on aquatic ecosystems and human life. This pollution will reduce the quality of the waters so that the biota living in the aquatic environment will also be threatened. This problem is getting worse because the dye is biologically difficult to decompose, so the polluted dye must be reduced in concentration and removed from the aquatic environment (El-Mekkawi et al., 2016).

One of the synthetic dyes that are harmful to health is methylene blue. Methylene blue (MB) is a basic dye that is relatively cheap compared to other dyes, so it is often used in chemistry, biology, medicine, and the coloring industry (Sagita et al., 2021). Methylene blue (Figure 1) is a cationic dye that is soluble in water. These dyes may cause eye irritation and skin, systemic effects including blood changes. In addition, exposure to methylene blue at certain levels can cause vomiting, nausea, diarrhea, dizziness, excessive sweating, and digestive inflammation (Wei et al., 2015).

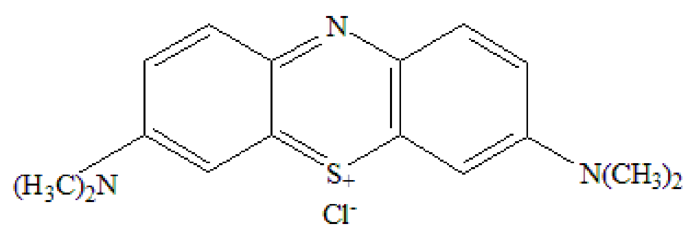

Figure 1. Methylene Blue (MB)

The negative impact of the use of dyes resulted in dye waste being processed first before being discharged into the environment (Kulkarni and Kaware, 2014). Wastewater treatment aims to eliminate or reduce the content of dissolved and dispersed pollutants in the wastewater solution. One way that can be done to treat wastewater is by adsorption (Alagha et al., 2020). Adsorption is a physical method that is widely used to treat waste because it is easy, efficient, and can use various types of adsorbents (Xu et al., 2021). One of the adsorbents that can be used to absorb dyes is layered double hydroxide (LDH) (Zubair et al., 2018).

LDH is a material consisting of a positively charged layer of 2-dimensional (2D) brucite. The presence of a network of hydrogen bonds between LDH layers results in the accumulation of layers, resulting in LDH in bulk form which has a 3-dimensional (3D) character. LDH has unique characteristics such as being easy to synthesize, having anions between layers that are easily exchanged, and having a large surface area (Xu et al., 2021). LDH also has a positive total charge so it is often used as an adsorbent (Benicio et al., 2015). LDH have the general formula: $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}.nH_2O$ where M^{2+} and M^{3+} are two and three valent metals, n is the mole fraction $M^{3+}/(M^{3+}+M^{2+})$ and A are balancing anions between layers (Karami et al., 2019). The coprecipitation method can be used in the LDH synthesis process. The ratio used is 3:1 (M^{2+}:M^{3+}) because LDH is known as a hydrotalcite material.

The effectiveness and efficiency of the material are the basis for selecting the use of a particular material. Besides the abundance of quality products, there is also a large buildup of chemical waste. The need to reuse and recycle materials such as composites is one of the best solutions. LDH has poor structural stability so it is necessary to modify LDH to produce composites. Modification of LDH can be done using graphene (Vinsiah et al., 2020), humic acid (Li et al., 2020a), biochar (Huang et al., 2019), hydrochar (Jung et al., 2021), and chitosan (Siregar et al., 2021a).

Chitosan is a derivative of chitin with the structure [β-(1→4)-2-amine-2-deoxy-D-glucose] (Zeng et al., 2015). Chitosan is a type of cationic polysaccharide biosorbent (Zhang et al., 2020). LDH has a less than optimal ability in the absorption process of cationic species so it is necessary to modify LDH with chitosan. The advantages of chitosan such as having NH_2 and OH functional groups that can help increase the absorption of cationic species because there will be interactions between the functional groups in chitosan and functional groups in cationic species such as methylene blue. Siregar et al. (2021a) reported that Mg/Al-chitosan was able to adsorb congo red dye with a maximum capacity of 344.828 mg/g. Research conducted by Khalili et al. (2021) reported that MnFe/chitosan showed a non significant decrease for four consecutive cycles of sunset yellow (SY) dye removal of 94.23%, 85.87%, 79.26%, and 61.98%, respectively.

In this study, modification of LDH using chitosan aims to increase the surface area of the material so that the adsorption capacity obtained also increases, that the structure of the material is more stable so that it can be used repeatedly in the process of removing methylene blue dye in water. The synthesized materials were characterized using XRD, FTIR, and BET analysis. In this study, the selectivity of a mixture of various dyes was carried out to determine the most selective dyestuff. The most selective dyes for each adsorbent will be subjected to adsorption studies including kinetic, isotherms, and thermodynamics, as well as adsorbent regeneration studies.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Instrumentation

The materials used in this study were $Mg(NO_3)_2.6H_2O$ (EMSURE ®), $Al(NO_3)_3.9H_2O$ (Sigma-Aldrich), chitosan extract ed from shrimp shells, NaOH, distilled water, nitrogen, rhoda mine-B (Rh-B), malachite green (MG), and methylene blue (MB). The synthesized material was characterized using X-Ray Rigaku Miniflex-6000, FTIR by Shimadzu Prestige-21, and Adsorption–desorption N_2 analysis was performed using a Quantachrome Micromeritics ASAP surface area and porosity analyzer, as well as adsorption analysis using UV-Visible Bio-Base spectrophotometer BK-UV1800.

2.2 Synthesis of Mg/Al

The coprecipitation method with molar ratio (3:1) was used in the synthesis of Mg/Al-NO_3 LDH. $Mg(NO_3)_2.6H_2O$ (19.230 g, 100 mL) and $Al(NO_3)_3.9H_2O$ (9.378 g, 100 mL) were mixed and the pH was adjusted to 10 using 2 M NaOH. The mixture was stirred at 80°C for 17 hours and was used in atmospheric nitrogen conditions to minimize the formation of Mg/Al-CO_3 in the synthesis process. After 17 hours, the precipitate was filtered, rinsed, and dried. Materials were characterized using XRD, FTIR, and BET analysis.

2.3 Extraction of Chitosan

Demineralization and deproteination processes were carried out to extract shrimp shells. Shrimp shells were crushed and put into a beaker, then 1 M HCl was added in a ratio of 1:10 (w/v). The mixture was stirred at 60°C for 3 hours. After the stirring is complete, the precipitate is filtered and dried. After the demineralization process is complete, it is followed by the deproteination process. The residue from the demineralization process was put into a beaker and 0.1 M NaOH was added in a ratio of 1:10 (w/v). The mixture was stirred at 60°C for 1 hour. After 1 hour, the precipitate was filtered and dried in the oven. The chitosan obtained was characterized using XRD, FTIR, and BET to prove the success of extracting chitosan from shrimp shells.

2.4 Preparation of Mg/Al-chitosan

60 mL of a mixture of $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ solutions were stirred for 1 hour and the pH was adjusted to 10 using NaOH. After 1 hour, 3 g of chitosan was added to the mixture. Stirring was continued for up to 72 hours at 80°C. After completion, the precipitate was filtered, rinsed, and dried for characterization using XRD, FTIR, and BET analysis.

2.5 Selectivity Dyes (Rhodamine-B, Malachite Green, and Methylene Blue)

20 mg/L of each dye as much as 20 mL was added with 0.02 g of adsorbent. The mixture is stirred according to the predetermined contact variation. After the stirring was completed, the filtrate was measured at 500-700 nm using a UV-Visible spectrophotometer. The dye with the largest adsorption capacity is used in the next adsorption process.

2.6 Effect of Adsorption Contact Time

100 mg/L methylene blue (20 mL, 0.02 g adsorbent) adjusted the pH according to the optimum pH of methylene blue. The mixture was stirred according to variations in contact time (0, 5, 20, 30, 60, 90, 120, 150, 180, and 200 minutes) and the filtrate was measured using a UV-Visible spectrophotometer.

2.7 Effect of Concentration and Temperature

Variations in the initial concentration of methylene blue and variations in adsorption temperature were carried out to see the effect of isotherm and adsorption thermodynamics. The initial concentration variations (60, 70, 80, 90, and 100 mg/L) were 20 mL and 0.02 g of adsorbent was added. The mixture was stirred for 2 hours and using various temperatures (30, 40, 50, and 60°C). After 2 hours, the filtrate was measured using a UV-Visible spectrophotometer at a wavelength of methylene blue (664 nm).

2.8 Regeneration of Adsorbent

The regeneration process was carried out by adsorption of MB dye (100 mg/L, 25 mL) and adding 0.1 g of adsorbent. The solution was stirred and the filtrate was measured using a UV-Visible spectrophotometer. The adsorbate bound to the adsorbent will be released by a desorption process using an ultrasonic system, then the adsorbent is dried using an oven. The same treatment was carried out for the next cycle.

3. RESULTS AND DISCUSSION

Figure 2(a) shows the diffraction pattern of Mg/Al where peaks appear at angles 11.47°(003), 22.86°(006), 34.69°(009), and 61.62°(110), the results obtained are similar to JCPDS data No. 22-700. Figure 2(b) shows the diffraction pattern of chitosan where peaks appear at an angle of 7.93°(003) and 19.35°(002) as reported by Mohadi et al. (2022) that the diffraction pattern of chitosan appears at an angle of 9.49°(001) and 19.59°(002). Peaks that appear at angles 10.83°(003), 19.52°(006), and 60.6°(110) indicates that Mg/Al-chitosan has a characteristic peak from each of its constituent materials, namely LDH and chitosan. This indicates that the Mg/Al-chitosan synthesis process was successful (Figure 2(c)).

Figure 3(a) shows the results of the FTIR analysis of Mg/Al which appears at 3500 cm^{-1} indicating OH vibrations from water molecules and at 1635 cm^{-1} stretching vibrations from OH occur. The N-O group from nitrate appears at a wavenumber of 1381 cm^{-1}. The peak that appears at 748 cm^{-1} indicates the presence of M-O vibrations. Figure 3(b) shows the spectrum of chitosan, where the strain vibrations of the NH_2 and OH groups occur at 3447 cm^{-1}. Spectrums that appeared at 1652 cm^{-1} and 1566 cm^{-1} indicated the presence of $CONH_2$ and NH_2 from chitosan. Figure 3(c) shows the results of Mg/Al-chitosan where the spectrum that appears at 1381 cm^{-1} is the vibration of the nitrate anion from LDH and the spectrum at 3447 cm^{-1} shows the strain of NH_2 and OH groups from chitosan (Mohadi et al., 2022).

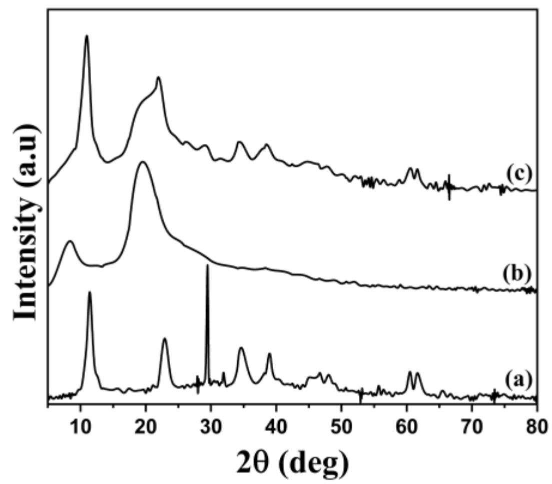

Figure 2. XRD Patterns of Mg/Al (a), Chitosan (b), and Mg/Al-chitosan (c)

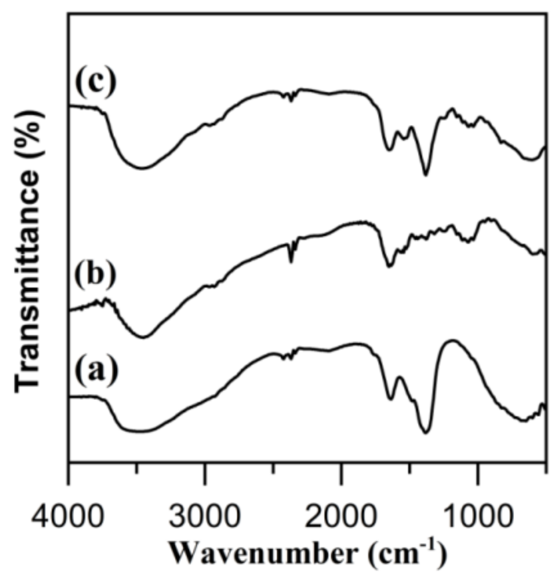

Figure 3. FTIR Spectra for Mg/Al (a), Chitosan (b), and Mg/Al-chitosan (c)

Important factors affecting the quality of the adsorbent are surface area, pore volume, and pore size. Analysis to determine surface area, pore volume, and pore size can be done using the BET method. BET theory is based on the adsorption process using the principle of adsorption isotherm (Langmuir

Table 1. BET Analysis of Materials

Materials	Surface Area (m^2/g)	Pore Volume (cm^2/g) BJH	Pore Size (nm), BJH
Mg/Al	5.845	0.017	17.057
Chitosan	8.558	0.018	16.983
Mg/Al-chitosan	24.556	0.031	3.169

Table 2. Kinetic Parameter

Adsorbent	Initial Concentration (mg/L)	Qe_{exp} (mg/g)	PFO			PSO		
			Qe_{calc} (mg/g)	R^2	k_1	Qe_{calc} (mg/g)	R^2	k_2
Mg/Al	100.608	40.919	10.044	0.901	0.032	41.322	0.999	0.012
Chitosan	100.608	45.421	1.262	0.901	0.023	45.455	0.999	0.057
Mg/Al-chitosan	100.608	46.877	2.757	0.922	0.037	46.948	0.999	0.029

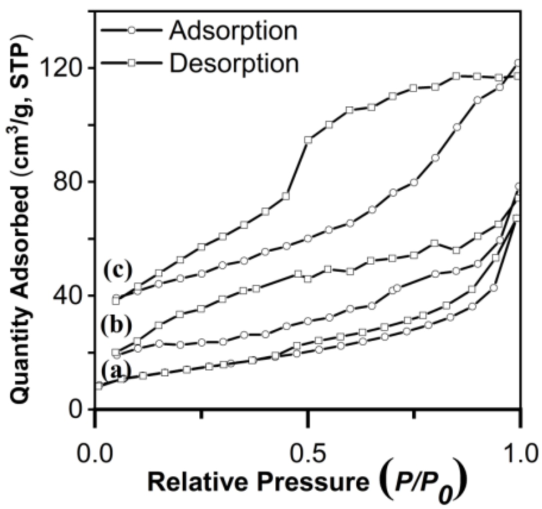

Figure 4. BET Profile of Mg/Al (a), Chitosan (b), and Mg/Al-chitosan (c)

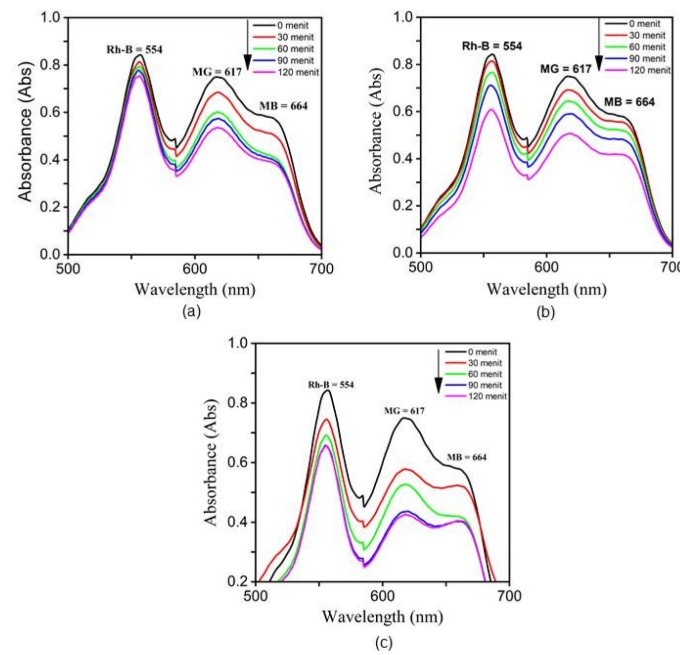

Figure 5. Selectivity of Rh-B, MG, and MB onto Mg/Al (a), Chitosan (b), and Mg/Al-chitosan (c)

theory). In the adsorption process, the system that occurs is gas-solid. Gases are adsorbed (adsorbate) and solids are adsorbents (adsorbent). The pore size of the adsorbent will be determined by the amount of gas absorbed. Based on the results of the BET analysis, the data obtained are as shown in Table 1. The surface area of Mg/Al is 5.845 m^2/g, the surface area of chitosan is 8.558 m^2/g, and the surface area of Mg/Al-chitosan has increased to 24.556 m^2/g. Figure 4 shows the adsorption-desorption pattern of each adsorbent following Type IV where the adsorption isotherm on mesoporous adsorbents with strong and weak affinities (Siregar et al., 2021b).

Figure 5 shows the selectivity of a mixture of rhodamine-B (Rh-B), malachite green (MG), and methylene blue (MB) dyes. In Figure 5, it can be seen that the longer the time used, the more significant the decrease in absorbance for MB dye. At 90-120 minutes it shows that there is an insignificant decrease in MB, this indicates that at 90-120 minutes MB has been in equilibrium.

Figure 6 shows a graph of the effect of contact time on the adsorption of methylene blue by the adsorbent, where the longer the adsorption contact time, the greater the methylene blue adsorbed. The results showed that each adsorbent optimally adsorbed methylene blue at 90 minutes, but if it is too long it can reduce the absorption rate. The longer the contact time can also lead to desorption, namely the release of dye

Table 3. Isotherm Adsorption

Adsorbent	Adsorption Isotherm	Adsorption Constant	303K
Mg/Al	Langmuir	Q_{max}	84.746
		kL	0.017
		R^2	0.7454
	Freundlich	n	2.05
		kF	13.527
		R^2	0.6056
Chitosan	Langmuir	Q_{max}	89.286
		kL	0.018
		R^2	0.9862
	Freundlich	n	1.458
		kF	7.525
		R^2	0.5047
Mg/Al-chitosan	Langmuir	Q_{max}	108.696
		kL	0.36
		R^2	0.8959
	Freundlich	n	2.181
		kF	18.655
		R^2	0.6207

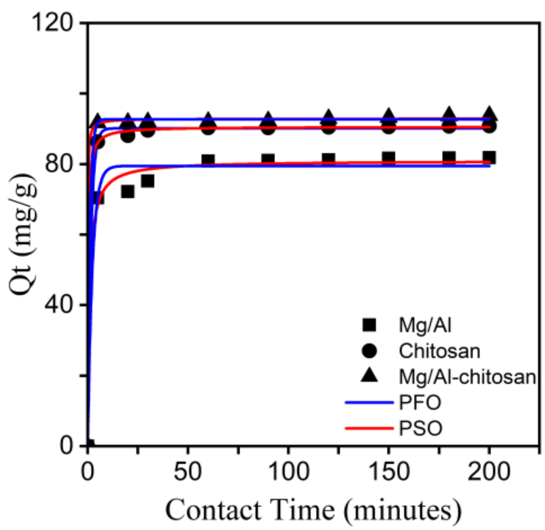

Figure 6. Variation of Adsorption Contact Time

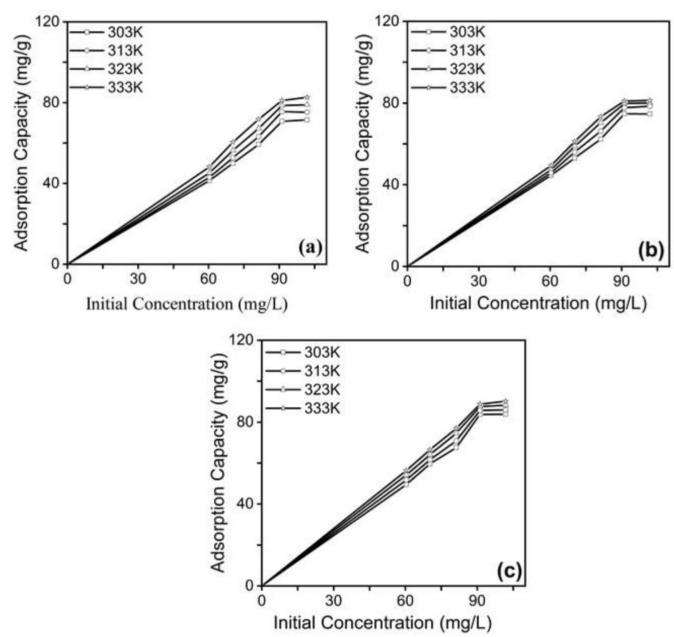

Figure 7. Effect of Initial Concentration and Adsorption Temperature of Mg/Al (a), Chitosan (b), and Mg/Al-chitosan (c)

that has been bound by the adsorbent. Bernard and Jimoh (2013) showed that after the adsorption reached equilibrium at the optimum contact time, the further addition of contact time between the adsorbent and the adsorbate did not have a significant effect on the absorption of the dye.

The determination of the equilibrium model depends on the value of the correlation coefficient (R^2). A suitable equilibrium model is an equilibrium model with a value of (R^2) that is higher or closer to 1 (Seedao et al., 2018; Juleanti et al., 2021). The value of the correlation coefficient (R^2) of the second order is closer to one (1) than the first order. If the value of (R^2) in pseudo first order (PFO) is greater and closer to the value of 1 then the adsorption involves a physical reaction and if the value of (R^2) in the pseudo second order (PSO) is greater and closer to the value of 1 then the adsorption involves

Table 4. Thermodynamic Adsorption

Adsorbent	T (K)	Q_e (mg/g)	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
Mg/Al	303	41.416	16.487	0.061	-1.873
	313	43.053			-2.479
	323	45.237			-3.085
	333	48.208			-3.691
Chitosan	303	44.6	12.669	0.05	-2.558
	313	45.843			-3.06
	323	47.238			-3.563
	333	49.36			-4.065
Mg/Al-chitosan	303	49.572	31.703	0.117	-3.694
	313	51.756			-4.862
	323	54.211			-6.03
	333	56.394			-7.198

Table 5. Adsorption Capacity using Several Adsorbents

Adsorbent	Adsorption Capacity (mg/g)	Reference
Chitosan/zeolite Composite	24.51	(Dehghani et al., 2017)
H_2SO_4 Cross-linked Magnetic Chitosan Nanocomposite Beads	20.41	(Rahmi and Mustafa, 2019)
Fe_3O_4 Activated Montmorillonite Nanocomposite	106.4	(Chang et al., 2016)
Chitosan Resin	11.3	(Buaphean et al., 2017)
Chitosan	11.04	(Moosa et al., 2016)
Activated Lignin Chitosan	36.25	(Albadarin et al., 2017)
N,O-carboxymethyl Chitosan	1.14	(Sulizi and Mobarak, 2020)
Ultrasonic Surface Modified Chitin	26.69	(Dotto et al., 2015)
Carbon Physical Activation	15.553	(Khuluk, 2019)
Dried Cactus (DC)	14.045	(Sakr et al., 2020)
Natural Cactus (NC)	3.435	(Sakr et al., 2020)
Chitosan/organic Rectorite-Fe_3O_4	24.69	(Zeng et al., 2015)
Natural Zeolite	21.189	(Ngapa and Gago, 2021)
Micro Cellulose Fibrils	54.9	(Kankilic and Metin, 2020)
Rice Husk	25	(Patil et al., 2017)
Mg/Al	84.746	This Work
Chitosan	89.286	This Work
Mg/Al-chitosan	108.696	This Work

a chemical reaction (Wang et al., 2013). The adsorption rate data in Table 2 shows that the PSO model provides a more presentable model of the adsorption rate, the second-order equation is based on the assumption that adsorption involves a chemical process between the adsorbent and the adsorbate (Hamzezadeh et al., 2022).

The adsorption isotherm was determined to determine the relationship between the concentration of the adsorbed substance (adsorbate) and the amount absorbed at a constant temperature. There are two types of isotherms commonly used to determine the type of adsorption, namely the Langmuir isotherm and the Freundlich isotherm (Seedao et al., 2018). The determination of the Langmuir isotherm is done by making a relationship curve between C_e and C_e/Q_e, so that the C_e versus C_e/Q_e curve is obtained. While the determination of the Freundlich isotherm is done by making a curve of the relationship between log C_e and log Q_e (Amtul et al., 2018).

Figure 7 shows a linearization graph for the adsorption of each adsorbent on methylene blue. This is indicated by the value of the linear regression coefficient (R^2) on the Langmuir isotherm is greater than the Freundlich isotherm so that the adsorption pattern that occurs on each adsorbent with methylene blue dye is monolayer with the Langmuir isotherm model (Zhang et al., 2020). The adsorption capacities of Mg/Al, chitosan, and Mg/Al-chitosan were 84.7466 mg/g, 89.286 mg/g, and 108.696 mg/g as shown in Table 3. The results showed that Mg/Al-chitosan was the most effective adsorbent to absorb MB.

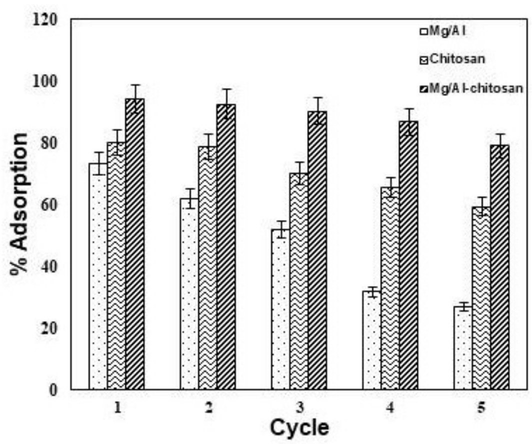

Figure 8. Regeneration of Mg/Al (a), Chitosan (b), and Mg/Al-chitosan (c)

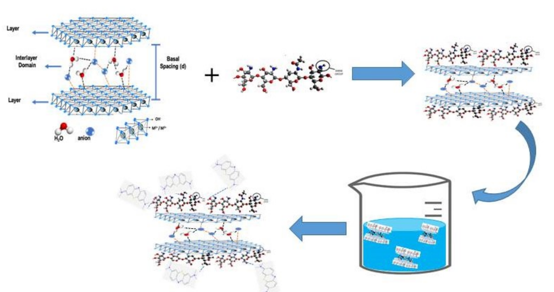

Figure 9. Adsorption Mechanism of Methylene Blue using Mg/Al-chitosan

Thermodynamic parameters are needed to provide information related to the direction and changes in internal energy that occur during the adsorption process of methylene blue with the adsorbent including the enthalpy change (ΔH) (Ge and Du, 2020), the entropy change (ΔS) (Ali et al., 2020), and the Gibbs free energy change (ΔG) (Zhu et al., 2012; Mohadi et al., 2022). Based on Table 4, it can be seen that the energy released during the methylene blue adsorption process is highly dependent on the type of adsorbent interaction. The positive enthalpy parameter value (ΔH) stated in Table 4 indicates that the adsorption process of methylene blue occurs endothermic where the adsorption capacity at the same initial concentration increases with increasing temperature (Li et al., 2020b). The small entropy value (ΔS) indicates that the distribution of methylene blue on the adsorbent surface is very regular with a small entropy value (Patil et al., 2017). The value of Gibbs free energy (ΔG) is negative, indicating that the adsorption process of methylene blue takes place spontaneously (Wang et al., 2013).

The regeneration process of the adsorbent aims to see the ability to reuse the adsorbent which will be used for the re-adsorption process. Regeneration aims to restore the function of the active site of the adsorbent so that it can bind the adsorbate again and there is a rearrangement of the groups of the adsorbent that have been used in the adsorption process. Figure 8 shows that Mg/Al and chitosan decreased drastically from cycles 3-5, while Mg/Al-chitosan showed an insignificant decrease in adsorption capacity from cycles 1 to 5. This indicates that Mg/Al-chitosan is an effective adsorbent used repeatedly in the process of removing MB dye from water.

The adsorption mechanism of methylene blue using Mg/Al-chitosan is shown in Figure 9. Figure 9 shows the presence of functional groups of chitosan in the form of NH_2 and OH bonded to methylene blue, thus the dye tends to bind more strongly to the OH group of chitosan, so that the binding of methylene blue on the adsorbent is more dominant in chemical adsorption, which is supported by the data. adsorption isotherm.

A comparison of the adsorption capacity of methylene blue using various adsorbents is shown in Table 5. Table 5 shows that Mg/Al-chitosan in this study was able to adsorb methylene blue with the largest capacity compared to others, namely 108.696 mg/g.

4. CONCLUSION

This study aims to modify the LDH using chitosan, as evidenced by XRD analysis where the peaks that appear in Mg/Al-chitosan are similar to the typical peaks of the constituent materials, namely Mg/Al and chitosan. This is confirmed by FTIR analysis where the spectrum that appears in Mg/Al-chitosan is similar to the spectrum in Mg/Al and chitosan. As well as BET analysis where there is an increase in the surface area of Mg/Al after being modified to Mg/Al-chitosan from 5.845 m^2/g to 24.556 m^2/g. In the dye selectivity process, MB tends to be more easily absorbed than Rh-B and MG. In this study, the adsorption process followed the Langmuir isotherm equation. The thermodynamic data showed that the adsorption process was endothermic, regular, and spontaneous. The regeneration process confirmed that Mg/Al-chitosan is an effective adsorbent for repeated use in the MB adsorption process.

5. ACKNOWLEDGEMENT

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