Synthesis of Mg/Al–Citric Acid Hydrotalcite and Its Application as an Adsorbent for Crystal Violet Dye

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Abstract

Crystal violet is a synthetic dye widely used in the textile industry and has the potential to cause environmental pollution if discharged directly into water bodies without proper treatment. One effective method for dye removal is adsorption using hydrotalcite as an adsorbent. This study aimed to synthesize and characterize Mg/Al-citric acid hydrotalcite and to evaluate its adsorption performance toward crystal violet. Mg/Al-citric acid hydrotalcite was successfully synthesized using the coprecipitation method followed by a hydrothermal process at 120 °C for 20 hours and characterized using FTIR and XRD. The adsorption study was carried out using the batch method, and the optimum conditions were obtained at pH 6, contact time of 60 minutes, and crystal violet concentration of 80 mg/L. Kinetic analysis showed that the adsorption process followed the pseudo-second-order model with an R^2 value of 0.9996 and a rate constant (k) of 0.3186 mg/g·min, while the adsorption isotherm was best described by the Temkin isotherm model with an R^2 value of 0.9668. These results indicate that Mg/Al-citric acid hydrotalcite has good potential as an effective adsorbent for the removal of crystal violet from aqueous solution

Keywords: adsorption; adsorption kinetics; crystal violet; Mg/Al-citric acid hydrotalcite; Temkin isotherm

I. INTRODUCTION

Water pollution due to industrial waste disposal is one of the environmental problems that continues to be a concern, especially in the textile industry that produces liquid waste with dyes and organic compounds that are difficult to remove. Dyes are one of the important components in the textile production process because they determine the visual characteristics of the product. At the beginning of its development, the textile dyeing process made extensive use of natural dyes. However, industrial and technological developments have caused the use of synthetic dyes to be more widespread because they have high availability, diverse color variations, ease of application, and relatively stable color characteristics (Ali & Adriana, 2025). This stability allows synthetic dyes to maintain color intensity under various conditions, but at the same time cause some dyes to be difficult to decompose after entering the environment (Pujilestari, 2015).

One of the synthetic dyes that can be found as contaminants in liquid waste is violet crystals. Violet crystals are cationic dyes that have a complex aromatic structure and are relatively stable so that their presence in the environment can be a problem if not handled properly. Dye compounds that enter water bodies not only affect the visual quality of water, but can also interfere with light penetration and photosynthesis processes of aquatic organisms. In addition, some organic compounds contained in dye waste have toxic potential and can pose a risk to organisms and human health if exposed to certain concentrations and conditions (Berradi *et al.,* 2019; Maryani *et al.,* 2025). These characteristics show the importance of developing treatment methods that are able to effectively remove dyes from water.

Various methods have been developed to deal with dye-containing waste, including photocatalysis, solvent extraction, membrane filtration, ion exchange, electrochemical processes, bioremoval, and adsorption. Each method has different mechanisms and limitations, especially related to energy requirements, operational costs, process complexity, and the potential for by-product formation. Among these methods, adsorption is widely used in water treatment because the process is relatively simple, can be performed under mild operating conditions, and allows the use of various materials as adsorbents (Zhou et al., 2014). The effectiveness of adsorption is influenced by the characteristics of the adsorbent and the process conditions, such as the pH of the solution, the time of contact, the mass of the adsorbent, and the initial concentration of the dye. Optimization of these parameters is necessary because changes in operating conditions can affect the interaction between the adsorbate and the surface of the adsorbent as well as determine the capacity and efficiency of dye removal (Tangio, 2013; Maryani *et al.,* 2025).

The development of layered material-based adsorbents is one of the interesting approaches in the adsorption process. One of the materials that is widely studied is hydrotalcytes, which are a group of layered double hydroxides (LDHs) which are generally composed of divalent and trivalent metal cations with anions located in the interlayer region to maintain charge neutrality. The Mg/Al system is one of the composition of hydrotalcytes that is widely studied because of its structural characteristics and ion exchange properties. Hydrotalcytes have a number of characteristics that support their use as a functional material, including layered structures, the presence of active sites, the ability to exchange anions, and flexibility in modifying the composition and anions between layers (Cavani *et al.,* 1991; Kloprogge *et al.,* 2002). These characteristics cause hydrotalcyte to have the potential to be applied as an adsorbent or supporting material in various environmental treatment processes.

The performance of hydrotalcytes as an adsorbent can be influenced by the composition of the metal, the ratio of molar cations, the type of interlayer anions, and the synthesis method used. Modification of the structure of hydrotalcytes by including certain organic anions in the interlayer region can change the surface characteristics and the interaction of the material with the target molecule. One of the compounds that has the potential to be used as a modified anion is citric acid. Citric acid has several carboxylic groups that can interact with the surface of the material as well as the species in the solution. Therefore, the presence of citric acid in the material structure has the potential to affect the surface properties and the interaction of hydrotalcyte adsorption with dyestuffs.

Several previous studies have demonstrated the potential of Mg/Al hydrotalcytes in the process of adsorption of contaminants from the environment. Wiyantoko *et al.* (2014), for example, reported the use of Mg/Al hydrotalcytes with a molar ratio of 2:1 to adsorb Cr(VI), with an optimal adsorption capacity of 55.57 mg/g. These results suggest that Mg/Al hydrotalcytes have the ability to interact with anionic species in solution and can be utilized as adsorbent materials. However, the adsorption characteristics of hydrotalcytes can differ depending on the type of adsorbate, material composition, interlayer anions, and process conditions. Thus, the results of studies on certain metal ions or contaminants cannot be directly used to describe the behavior of materials to cationic dyes such as violet crystals.

The use of hydrotalcites modified with organic anions is also an interesting approach to improve the suitability of material characteristics to the target molecule. However, studies on Mg/Al hydrotalcites modified using citric acid as an adsorbent material for violet crystal removal still need to be developed, especially in relation to the effect of adsorption conditions on the material's ability to remove dyestuffs. This is the basis for research that examines the relationship between the material characteristics of Mg/Al-citric acid and the conditions of adsorption operation on violet crystals.

In this study, Mg/Al-citric acid hydrotalcytes were synthesized using the coprecipitation method followed by hydrothermal treatment. Citric acid was used as an organic anion to

modify Mg/Al hydrotalcyte material. The adsorption process was studied through pH variations, contact time, adsorbent mass, and initial concentration of violet crystals to obtain appropriate adsorption conditions. Thus, this study aims to synthesize and evaluate the performance of Mg/Al-citric acid hydrotalcytes as violet crystal adsorbents and determine the effect of adsorption conditions on the ability to remove these dyes.

II. METHOD

A. Materials and instruments

The materials used in this study are crystal violet (analytical grade), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, analytical grade), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, analytical grade), citric acid (analytical grade), sodium hydroxide (NaOH, analytical grade), hydrochloric acid (HCl, analytical grade), distilled water, deionized water, and nitrogen gas supplied by PT Samator.

The instruments used included analytical balances, magnetic stirrers, shakers, ovens, centrifuges, pH meters, mortars and pestles, as well as Whatman No. 42 filter paper (90 mm diameter). Characterization and quantitative analysis were carried out using the UV–Vis spectrophotometer (1601) for the determination of violet crystals, the MiniFlex 600 X-ray dyphractometer (XRD) for crystal structure analysis, and the Shimadzu IRSpiritX Fourier transform infrared spectrometer (FTIR) for the identification of functional groups.

B. Synthesis of Mg/Al-NO_3 and Mg/Al-citrate hydrotalcites

Mg/Al-NO_3 hydrotalcyte was synthesized by hydrothermal coprecipitation method with a molar Mg/Al ratio of 3:1 following the procedure reported by Dwiasi et al. (2020), with modification of the experimental composition. $Mg(NO_3)_2 \cdot 6H_2O$ (7.7 g) and $Al(NO_3)_3 \cdot 9H_2O$ (3.75 g) were dissolved separately in deionized water to a final volume of 100 mL for each solution. Both solutions were cleaned with nitrogen gas for 15 minutes to minimize carbonate contamination. The solution was then mixed and stirred for 30 minutes. A 0.50 M NaOH solution was added in droplets until the pH reached 10, followed by continuous stirring for 2 hours under a nitrogenous atmosphere. The resulting sludge is transferred into a PTFE container and undergoes hydrothermal treatment at 120 °C for 20 hours. The product is centrified at 2500 rpm for 15 minutes, filtered, and washed with deionized water until free of residual soluble species. The solids are then dried at 120 °C for 5 hours. The resulting material is marked with XRD and FTIR.

Mg/Al-citrate hydrotalcyte was synthesized using a similar hydrothermal coprecipitation procedure based on Handayani et al. (2014), with modifications. $Mg(NO_3)_2 \cdot 6H_2O$ (7.7 g) and $Al(NO_3)_3 \cdot 9H_2O$ (3.75 g) were dissolved separately in deionized water to 100 mL and purified with nitrogen gas for 15 minutes. The solution was combined and stirred for 30 minutes. Citric acid (0.015 mol; 3.15 g) was then added, followed by the addition of 0.50 M NaOH droplets until pH 10 was reached. The suspension was stirred continuously for 2 hours under a nitrogenous atmosphere and then underwent hydrothermal treatment at 120 °C for 20 hours. The product is centrifuged at 2500 rpm for 15 minutes, filtered, washed with deionized water, and dried at 120 °C for 5 hours. Mg/Al-citrate synthetic materials are characterized using XRD and FTIR to evaluate their crystal structure and functional groups.

C. Preparation of crystal violet calibration curve

The calibration curve is made using a standard solution of violet crystals with a concentration of 0; 1,0; 1,5; 2,0; 2,5; 3,0; 3,5; and 4.0 mg/L. The standard solution is made by diluting a 100 mg/L violet crystal parent solution using a 100 mL measuring flask. The absorbance of each solution is measured using a UV-Vis spectrophotometer at a maximum

wavelength of 590 nm. A calibration curve is created by plotting the absorbance against the concentration of the violet crystal and is used to determine the concentration of violet crystals remaining after the adsorption process.

D. Batch adsorption experiment

Batch adsorption experiments were conducted to determine the effect of pH, contact time, and initial concentration of violet crystals on the adsorption process. Unless otherwise stated, as much as 20 mg of hydrotalcite Mg/Al-citric acid was added to 15 mL of violet crystal solution and the adsorption process was carried out at room temperature.

1. Effect of pH

The effect of pH on adsorption was evaluated using 15 mL of crystalline violet solution with a concentration of 4 mg/L at pH variations of 4–11. pH adjustment was performed using HCl or NaOH solutions. A total of 20 mg of hydrotalcite Mg/Al-citric acid was added to the solution and beaten for 60 minutes at room temperature. After the adsorption process was completed, the adsorbents were separated from the solution by centrifugation at 4000 rpm for 15 minutes. The remaining concentration of violet crystals in the supernatant was determined using a UV-Vis spectrophotometer at a wavelength of 590 nm. The pH values that resulted in the highest adsorption performance were used as the optimal pH for subsequent experiments.

2. Effect of contact time

The effect of contact time was evaluated using 20 mg of hydrotalcite Mg/Al-citric acid and 15 mL of 4 mg/L solution of violet crystal at optimal pH. The mixture was shaken at room temperature with contact time variations of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 120 minutes. Once each contact time was reached, the adsorbents were separated from the solution by centrifugation at 4000 rpm for 15 minutes. The remaining concentration of violet crystals in the supernatant was determined using a UV-Vis spectrophotometer at a wavelength of 590 nm. The contact time that resulted in the highest adsorption performance was used as the optimal contact time.

3. Effect of initial crystal violet concentration

The effect of the initial concentration of violet crystals was evaluated using 20 mg of hydrotalcite Mg/Al-citric acid and 15 mL of violet crystal solution with concentrations of 1–10 mg/L at optimal pH and contact time. After the adsorption process was complete, the adsorbent was separated from the solution by centrifugation at 4000 rpm for 15 minutes. The concentration of violet crystals remaining in the supernatant was determined using a UV-Vis spectrophotometer at a maximum wavelength of 590 nm.

E. Adsorption kinetics

Adsorption results data on contact time variations were used to determine the adsorption kinetics of violet crystals in Mg/Al-citric acid hydrotalcytes. Adsorption kinetics were determined using first-order, second-order, pseudo-first-order, and second-order models. The first-order model was analyzed based on the equation $\ln C_t = -kt + \ln C_0$, while the second-order model was analyzed based on the equation $\frac{1}{C_t} = k_2 t + \frac{1}{C_0}$. The first-order pseudo-model was analyzed based on the equation $\log (q_e - q_t) = \log q_e - k_3 t$, while the second-order model was analyzed based on the equation $\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_4 q_e^2}$.

Based on the equation, C_0 is the initial concentration of the violet crystal, C_t is the concentration of the violet crystal at the time (t), q_e is the adsorption capacity at equilibrium, q_t is the adsorption capacity at the time (t), and t is the contact time. The value k is adsorption rate constants of the kinetics model used, respectively. The most suitable kinetic model is

determined based on the highest coefficient of determination (R^2) value obtained from linear regression

F. Adsorption Isotherms

Adsorption results data at initial concentration variations were used to determine the adsorption isothermal model that corresponded to the violet crystal adsorption system in Mg/Al-citric acid hydrotalcytes. Isothermal analysis was carried out using the Langmuir, Freundlich, Temkin, and Harkin-Jura models. The Langmuir isothermal model was analyzed using the $\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$, while the Freundlich isothermal model was analyzed using the equation $\log q_e = \log K_F + \frac{1}{n} \log C_e$. The Temkin isothermal model was analyzed using the equation $q_e = B \ln K_T + B \ln C_e$, with $B = \frac{RT}{b}$. The Harkin-Jura isothermal model was analyzed using the equation $\frac{1}{q_e^2} \frac{B}{A} - \left(\frac{1}{A}\right) \log C_e$.

Based on the equation, *C*e is the concentration of violet crystals at equilibrium (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant, K_F is the Freundlich constant, and *n* is the adsorption intensity parameter. In the Temkin model, *B* is the constant related to adsorption energy, *R* is the gas constant (8.314 J/mol K), *T* is the absolute temperature (*K*), *b* is the constant related to adsorption energy, and K_T is the Temkin constant. In the Harkin-Jura model, *A* and *B* are isothermal constants obtained from linear regression results.

The suitability of each isothermal model was determined based on the value of the determination coefficient (R^2) obtained from linear regression. The isothermal model with the highest R^2 value was used as the most suitable model to describe the adsorption characteristics of violet crystals in Mg/Al-citric acid hydrotalsite.

G. Penentuan presentase penurunan konsentrasi kristal violet

Persentase penurunan konsentrasi zat warna kristal violet ditentukan berdasarkan konsentrasi awal dan konsentrasi setelah adsorpsi yang diperoleh dari kurva kalibrasi berdasarkan nilai absorbansi. Persentase penurunan konsentrasi dihitung menggunakan persamaan berikut: Penurunan konsentrasi (%) $= \frac{C_0 - C_t}{C_0} \times 100\%$. C_0 adalah konsentrasi awal zat warna kristal violet dan *C*t adalah konsentrasi zat warna kristal violet setelah adsorpsi.

III. RESULTS AND DISCUSSIONS

A. Result

1. Synthesis of Mg/Al-NO_3 and Mg/Al-citrate hydrotalcites

Mg/Al-NO_3 and Mg/Al-citric acid hydrotalcytes were successfully obtained in the form of a white powder after the synthesis process. Visually, the two materials exhibit similar physical characteristics, as shown in **Figure 1** and **Figure 2.**



Figure 1. Mg/Al-NO_3 hydrotalcite

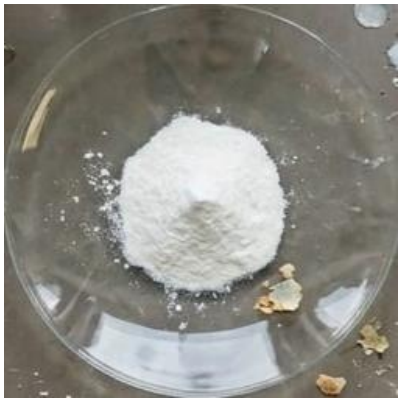


Figure 2. Mg/Al-citric acid hydrotalcite

2. FTIR Characterization

FTIR characterization yielded the infrared spectra of Mg/Al-NO_3 and Mg/Al-Citric Acid hydrotalcytes as shown in **Figure 3.** Both samples showed absorption bands in several wavenumber regions with a spectrum pattern showing the characteristics of each material.

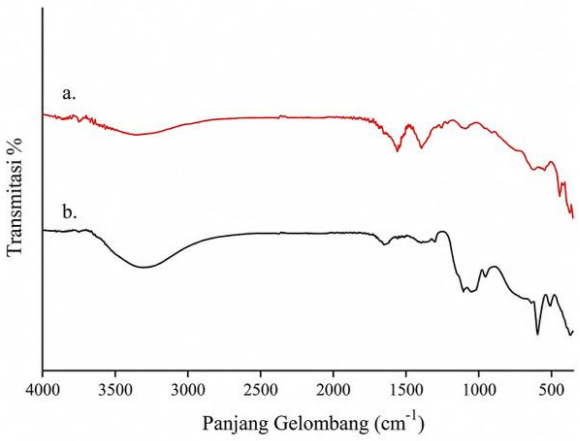


Figure 3. FTIR spectrum of hydrotalcytes (a) Mg/Al-Citric Acid and (b) Mg/Al-NO_3

Table 1. Comparison of Synthesis Results with FTIR Reference Hydrotalcyte Mg/Al-NO_3 and Hydrotalcite Mg/Al-Citric Acid.

Gugus fungsi	Number of Waves (cm^{-1})			
	Mg/Al-NO_3		Mg/Al-Citric acid	
	Synthesis results	References	Synthesis results	References
O-H ulur	3302,35	3456,44[a]	3353,93	3354[b]
O-H bend	1635,42	1635[c]		
NO_3^-	1301,60	1381[c]		
asymmetrical COO^-			1587,77	1567[b]
Symmetrical COO^-			1387,56	1386[b]

[a]Handayani *et al.,* (2015); [b]Perera *et al.,* 2015; [c]Dwiasi *et al.,* 2020

3. XRD Characterization

XRD characterization was carried out to determine the characteristics of the crystalline structure of hydrotalcytes Mg/Al-NO_3 and Mg/Al-Citric Acid. Measurements were made at an angle range of 2θ of 5–60°. The diffraction pattern of the two samples is shown in **Figure 4.** Hydrotalcytes Mg/Al-NO_3 showed peak diffraction at 2θ angles of 11.92°, 21.45°, and 35.05°. Meanwhile, Mg/Al-Citric Acid hydrotalcytes showed diffraction peaks at 2θ angles of 10.85°, 20.26°, and 34.44°.

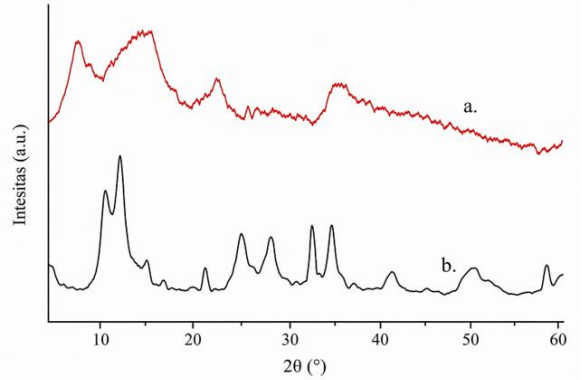


Figure 4. XRD Characterization of (a) Hydrotalcyte Mg/Al-Citric Acid and (b) Hydrotalcyte Mg/Al-NO_3

Table 2. Comparison of 2θ (°) between d(Å) hydrotalcytes Mg/Al-NO3 and hydrotalcytes Mg/Al-Citric Acid

Hydrotalcyte Mg/Al-NO_3		Hydrotalcyte Mg/Al-Citric Acid	
2θ (°)	*d* (Å)	2θ (°)	*d* (Å)
11,92	7,42	10,85	8,15
21,45	4,14	20,26	4,38
35,05	2,56	34,44	2,60

4. Violet Crystal Calibration Curve

The calibration curve of the violet crystal showed a linear relationship between concentration and absorbance in the concentration range of 0–4 mg/L. Based on the results of measurements using a UV-Vis spectrophotometer at a maximum wavelength of 590 nm, a linear regression equation of y = 0.1591x - 0.0171 was obtained with a determination coefficient value of R^2 of 0.9979.

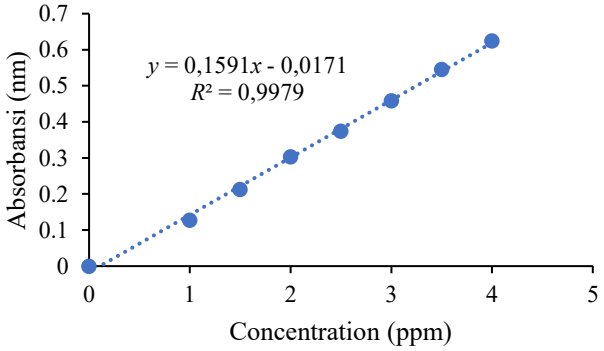


Figure 5. Violet Crystal Standard Solution Calibration Curve

5. Crystal Adsorption Study

5.1. Violet Effect of pH on Adsorption of Violet Crystals

The effect of pH on the adsorption of violet crystals using Mg/Al–citric acid hydrotalcytes is presented in **Figure 6.1.** The percentage of adsorption increases as the pH increases from 4 to the maximum value at pH 6. An increase in pH above 6 causes the percentage of adsorption to decrease. Based on these results, pH 6 is determined as the optimal condition for the adsorption of violet crystals.

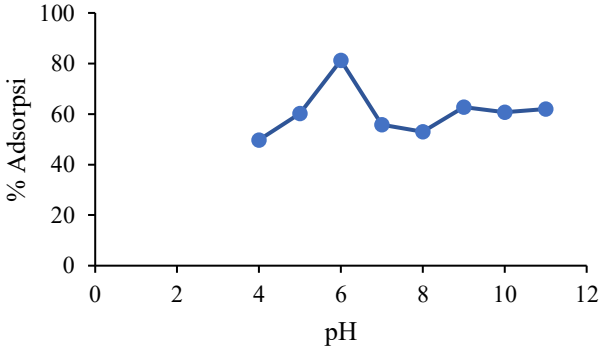


Figure 6.1. Effect of pH on Adsorption Percentage of Violet Crystals

5.2. Effect of Contact Time on Violet Crystal Adsorption

The effect of contact time on violet crystal adsorption is shown in **Figure 6.2.** The percentage of adsorption increases as the contact time increases and reaches a maximum value at the 60th minute of 81.3%. After the contact time exceeds 60 minutes, the percentage of adsorption does not show a significant increase and tends to decrease slightly.

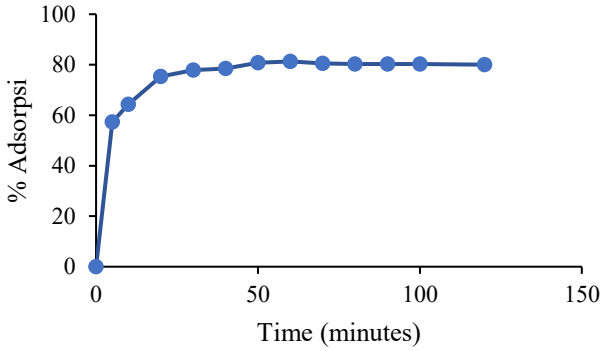


Figure 6.2. Effect of Time on Adsorption Percentage of Violet Crystals

5.3. Effect of Initial Concentration on Violet Crystal Adsorption

The effect of the initial concentration on the adsorption of violet crystals is presented in **Figure 6.3.** The highest percentage of adsorption was obtained at the initial concentration of 4 mg/L of 80.65%, with an adsorption capacity of 2.420 mg/g. At concentrations above 4 mg/L, the percentage of adsorption tended to decrease, while the adsorption capacity still increased.

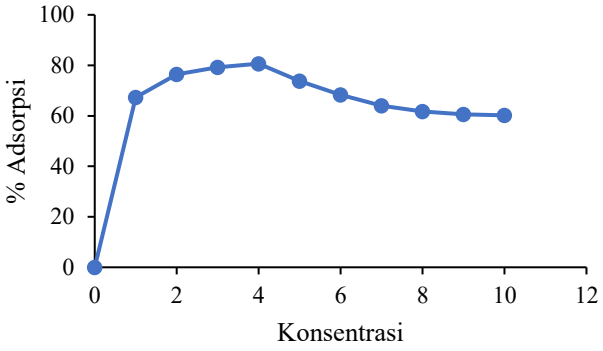
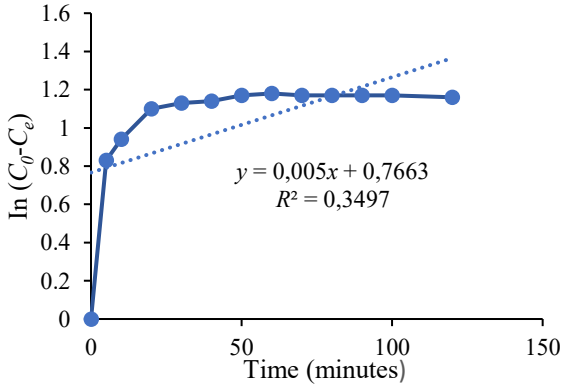
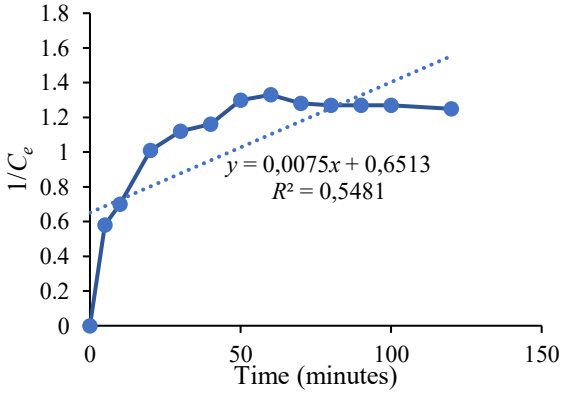


Figure 6.3. Effect of Concentration on Violet Crystal Adsorption Percentage

6. Adsorption Kinetics

The analysis of the adsorption kinetics of violet crystals using Mg/Al–citric acid hydrotalcite adsorbents was carried out by comparing four kinetic models, namely first-order, second-order, first-order, and second-order pseudo-stub. The linear regression graph of each model is shown in **Figure 7.** The results of the analysis show that the second-order pseudo-model has the highest determination coefficient (R^2) of 0.9996, with an adsorption rate constant (k) of 0.3186 $g \cdot mg^{-1} \cdot min^{-1}$. The linear equations, determination coefficient values, and adsorption rate constants of the four models are presented in Table 1.





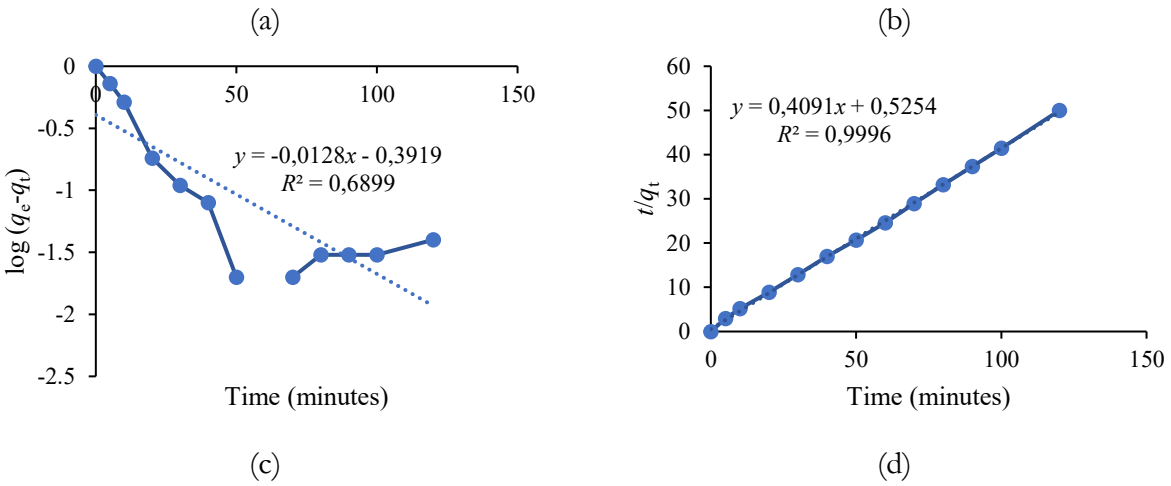


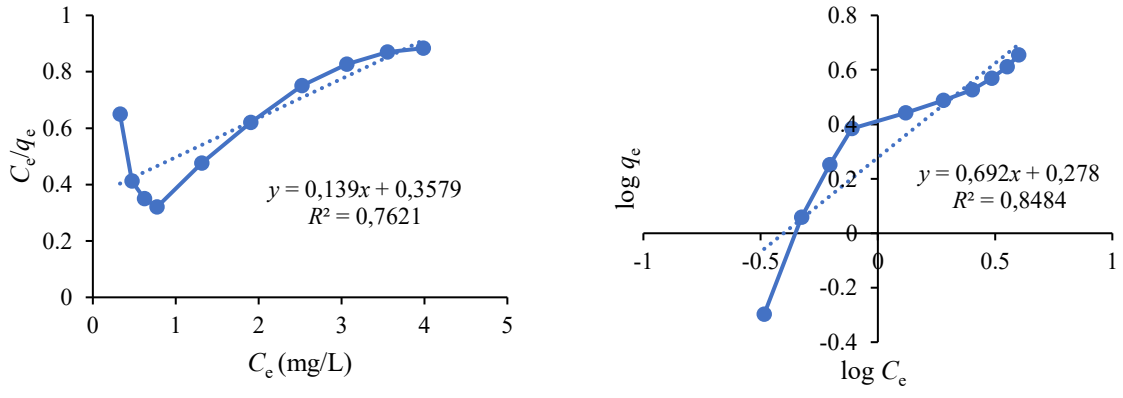
Figure 7. Graph of the Kinetics of Adsorption (a) Order One, (b) Order Two. (c) Pseudo Orde One and (d) Pseudo Orde Two

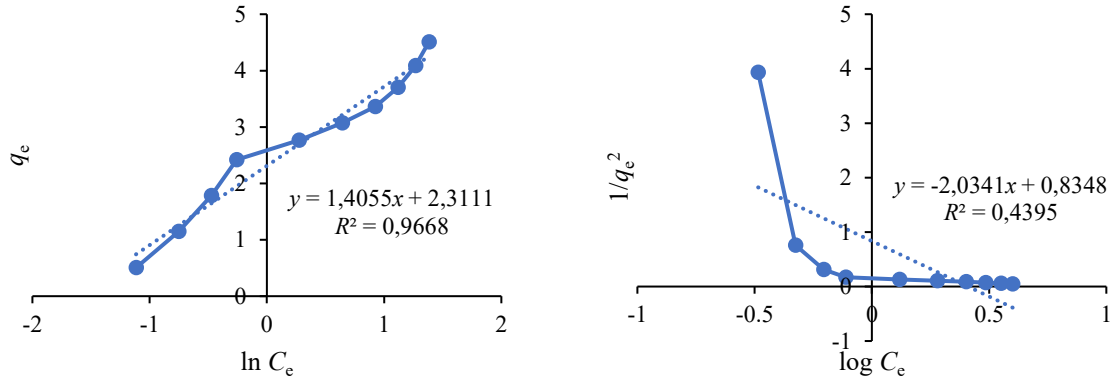
Table 3. Kinetics of Adsorption of Mg/Al-Citric Acid Hydrotalcite to Violet Crystals

Kinetics Model	Equation	R^2	k
Orde one	$y = 0{,}005x + 0{,}7663$	$R^2 = 0{,}3497$	0,005 minutes^{-1}
Orde two	$y = 0{,}0075x + 0{,}6513$	$R^2 = 0{,}5481$	0,0075 L·mg^{-1}·min^{-1}
Pseudo Orde One	$y = -0{,}0128x - 0{,}3919$	$R^2 = 0{,}6899$	0,0294 minutes^{-1}
Pseudo Orde Two	$y = 0{,}4091x + 0{,}5254$	$R^2 = 0{,}9996$	0,3186 g·mg^{-1}·min^{-1}

7. Adsorpsi Isotherm

The isothermal analysis of violet crystal adsorption using Mg/Al–citric acid hydrotalcite adsorbents was carried out using four models, namely Langmuir, Freundlich, Temkin, and Harkins–Jura. The graph of the results of the analysis of each model is shown in **Figure 8**, while the adsorption isothermal parameters are presented in Table 2. Based on the calculation results, the Temkin model produced the highest determination coefficient value (R^2) of 0.9668 compared to the Langmuir (0.7621), Freundlich (0.8484), and Harkins–Jura (0.4395) models.





(c) (d)

Figure 8. Isothermal Adsorption Graph of (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Harkin-Jura

Table 4. Comparison of Langmuir, Freundlich, Temkin and Harkin-Jura Adsorption Isotherms

Isotherm Model	R^2	q_m (mg/g)	K_L (L/mg)	E (kJ/mol)
Langmuir	0,7621	7,1942	0,3883	-29,66
	R^2	n	K_F (mg/g)	E (kJ/mol)
Freundlich	0,8484	1,4450	1,90	-33,60
	R^2	b_T (kJ/mol)	K_T (L/g)	E (kJ/mol)
Temkin	0,9668	1,76	5,18	-18,97
	R^2	A (mg/g)	B (mg/g)	
Harkin-Jura	0,4395	0,4916	0,4104	

B. Discussion

1. Synthesis of Mg/Al Hydrotalcytes and Interlayer Modification with Citric Acid

The coprecipitation method allows the formation of layered double hydroxide (LDH) through the deposition of metal cations under alkaline conditions. pH regulation plays an important role in the formation of hydroxide structures, while nitrogen flow during synthesis aims to minimize carbon dioxide contamination that can produce carbonate ions and interfere with the presence of nitrate anions in the interlayer space (Tazkia & Nurlieta, 2023; Suryaningsih *et al.,* 2021; Paryanto & Pranolo, 2011). Hydrothermal treatment also supports the formation and development of material crystalline structures (Safitri *et al.,* 2019).

Hydrotalcyte modification using citric acid aims to incorporate citrate anions into the interlayer structure. The larger size of the citrate anion compared to nitrate anion has the potential to cause changes in the distance between layers. These changes can be used as one of the indicators of successful modification of hydrotalcyte structure (Sari, 2018). Therefore, the success of modification is not only reviewed from the physical characteristics of the material, but also needs to be supported by the results of the characterization of its functional group and crystal structure.

2. Interpretation of FTIR and XRD Characterization

FTIR characterization provides information about the functional groups contained in the material as well as the chemical changes that occur after modification. The presence of hydroxyl groups and metal-oxygen bonds are characteristics that support the formation of hydrotalcite structures (Dwiasi *et al.,* 2020; Handayani *et al.,* 2015). In materials modified with citric acid, the appearance of absorption bands related to carboxylic groups indicates the presence of citrate components in the material. The difference in absorption characteristics between the two materials supports the chemical composition changes after the addition of citric acid (Perera *et al.,* 2015; Frost *et al.,* 2005).

The information is reinforced by XRD characterizations used to evaluate the crystalline structure and interlayer spacing of hydrotalcytes. The shift of the diffraction crest after modification indicates a change in the interlayer structure, while the presence of a typical LDH crest indicates that the basic characteristics of the structure are still identified. Changes in intensity and crest widening may also indicate changes in crystal regularity after modification. These findings are in line with the structural characteristics of LDH reported in previous studies (Putri *et al.,* 2023; Dwiasi *et al.,* 2020).

Overall, the results of FTIR and XRD are complementary in evaluating hydrotalcite modifications using citric acid. FTIR provides information on changes in functional groups, while XRD shows changes in crystal structure and spacing between layers. The combination of these two characterizations supports changes in material structure after the addition of citric acid, although the identification of successful intercalation requires more convincing consideration of the overall characterization data.

3. Suitability of Violet Crystal Concentration Measurement

The measurement of violet crystal concentrations using UV-Vis spectrophotometry is based on the relationship between solution concentration and absorbance. The use of maximum wavelengths aims to obtain an optimal absorption response so that concentration measurements can be performed with adequate sensitivity (Zein *et al.,* 2023; Sahumena *et al.,* 2020). The linearity of the calibration curve is an important aspect because its regression equations are used to estimate the concentration of violet crystals after adsorption. Good linear relationships support the use of such methods to evaluate concentration changes during the adsorption process (Sufyani & Sukesi, 2005).

4. Effect of pH on Adsorption of Violet Crystals

The pH of the solution affects adsorption because it can change the ionization state of the adsorbate and the surface charge characteristics of the adsorbent. These changes determine the interaction between the dye and the active site on the surface of the material (Crini, 2006; Foo & Hameed, 2010). In this system, the optimal pH conditions indicate the presence of the solution state that is most favorable for the interaction between the Mg/Al–citric acid hydrotalcyte and the violet crystal

Under conditions that are too acidic, hydrogen ions can compete with adsorbed species in interacting with the active site. The protonation of the groups on the surface of the adsorbent also has the potential to affect electrostatic interactions with violet crystals that are cationic in nature (Rafatullah *et al.,* 2010; Ferreira *et al.,* 2015). In contrast, changes in solution conditions at higher pH can affect the surface properties of the adsorbent and the interactions that take place during adsorption (Miyah *et al.,* 2016). Thus, changes in adsorption efficiency at pH variations suggest that the success of this process is determined not only by the presence of the adsorbent, but also by the chemical conditions of the solution.

5. Effect of Contact Time on Adsorption

Contact time is related to the opportunity for the adsorbate molecule to interact with the adsorbent active site. In the early stages, the adsorption process can proceed faster because there are still many active sites available. As the process progresses, the active site is gradually occupied by the adsorbate molecule so that the absorption rate may decrease as the system approaches equilibrium (Safrianti *et al.,* 2012).

The tendency of adsorption changes after the optimal contact time may be related to the increasingly limited available active sites or the possibility of desorption of some molecules that have previously been adsorpted (Murtihapsari *et al.,* 2012). Therefore, the determination of the optimal contact time is necessary to obtain effective operating conditions without excessively prolonging the process.

6. Effect of Initial Concentration on Adsorption

The initial concentration of the adsorbate affects the difference in concentration between the solution and the surface of the adsorbent, which can be the driving force for the movement of molecules towards the active site. An increase in the initial concentration can increase the number of molecules available for adsorption. However, when the number of adsorbate molecules increases compared to the availability of the active site, the adsorbent's ability to proportionately remove dyes from the solution may be limited.

The difference between the percentage of adsorption and the adsorption capacity needs to be considered in evaluating the performance of the material. The percentage of adsorption describes the proportion of dyes that are successfully removed from the solution, while the adsorption capacity indicates the amount of adsorbate absorbed per unit of adsorbent mass. Therefore, the conditions with the highest percentage of absorption are not necessarily identical to the conditions that produce the highest adsorption capacity. Both parameters need to be considered according to the purpose of using the adsorbent.

7. Interpretation of Adsorption Kinetics

Kinetic analysis was used to evaluate the model that was most suitable in describing adsorption changes over time. Model suitability was determined by comparing the ability of each equation to represent experimental data. In this study, the second-order pseudo-model provided a better match than other kinetic models tested.

A pseudo-order two-order model describes the rate of adsorption based on the relationship between the amount of adsorbed adsorption and the adsorption capacity in the equilibrium state (Ho & McKay, 2000). The similarity of this model suggests that a pseudo-order two equation can represent the kinetic behavior of the system under study. However, the mathematical fit of a model does not directly prove that adsorption takes place through a chemomorphy mechanism. The determination of the mechanism requires other supporting evidence in addition to the value of the determination coefficient. The obtained rate constant can also be used to describe the characteristics of the adsorption rate under the experimental conditions used (Baunsele & Missa, 2020).

8. Interpretation of Adsorption Isotherms

The isothermal model is used to describe the relationship between the amount of adsorbate bound to the adsorbent and the concentration of the adsorbate in the solution at equilibrium. The selection of a suitable model is important to explain the equilibrium characteristics of adsorption because the behavior of each system can be influenced by the properties of the adsorbent, the properties of the adsorbate, the surface area, the concentration, and the temperature (Handayani & Sulistyono, 2009; Al-Ghouti & Da'ana, 2020).

A comparison of the Langmuir, Freundlich, Temkin, and Harkins–Jura models shows that the Temkin model is best suited to describing the equilibrium data in this study. The Langmuir model is generally used to describe adsorption on surfaces assuming an equivalent adsorption site, while the Freundlich model is used to describe adsorption on heterogeneous surfaces. The Temkin model considers changes in adsorption heat as surface coverage increases due to the interaction between adsorbents and adsorbate (Atkins, 1999; Foo & Hameed, 2010; Ayawei *et al.,* 2017).

The fit of the Temkin model shows that the approach is best able to represent the equilibrium data obtained compared to the other models tested. However, the selection of models based on mathematical matches is not sufficient to ensure the homogeneity of the surface, the number of adsorption layers, or the definitive interaction mechanism. Such interpretations need to take into account the assumptions of each model and are supported by additional characterization or experimentation if necessary (Al-Ghouti & Da'ana, 2020).

9. Potential of Mg/Al–Citric Acid Hydrotalcite as an Adsorbent

Overall, the results showed that Mg/Al–citric acid hydrotalcytes were able to reduce the concentration of violet crystals in the solution. Adsorption performance was influenced by the relationship between material characteristics and process conditions, including solution pH, contact time, and initial adsorbate concentration. FTIR and XRD characterizations provided information on changes in functional groups and material structure, while adsorption testing showed their ability to absorb dyestuffs.

The results of kinetic and isothermal analyses further help explain the adsorption behavior over time and equilibrium conditions. Considering the overall findings, Mg/Al–citric acid hydrotalcite has the potential to be used as an adsorbent material to lower the concentration of violet crystals in the solution. However, further evaluation on variations in operating conditions and the use of more complex solutions is needed before their application is further developed.

IV. CONCLUSION

Mg/Al-NO_3 hydrotalcytes and Mg/Al-citric acid hydrotalcytes were successfully synthesized using the coprecipitation method with a mole ratio of Mg^{2+}:Al^{3+} of 3:1 at pH 10 and a hydrothermal temperature of 120 °C for 20 hours. The results of FTIR and XRD characterization showed the intercalation of some citrate anions into the hydrotalcyte structure, which was characterized by the appearance of a carboxylate group absorption band (COO^-) and an increase in the interlayer distance from 7.42 Å to 8.15 Å. Adsorption of violet crystals using Mg/Al-citric acid hydrotalcytes achieved optimal conditions at pH 6, contact time of 60 minutes, and an initial concentration of 4 mg/L, with a percentage reduction in concentration of 80.6%. The adsorption process followed a second-order pseudo-kinetics model with an R^2 value of 0.9996 and a Temkin isothermal model with an R^2 value of 0.9668, indicating that the model was the most consistent with the experimental data among the models tested.

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