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Optimization of Zn/Al-Oxalate Hydrotalcite as an Environmentally Friendly Adsorbent for Dye Waste Processing

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Abstract

Methylene blue is a synthetic dye commonly used in the textile industry. Methylene blue waste that is discharged into water bodies without treatment causes environmental pollution. One method of waste treatment is adsorption. Hydrotalcite is an anionic clay consisting of stacked positively charged layers, usually divalent (+2) and trivalent (+3) metal cations, and has anions between the layers. This study aims to determine the synthesis method of Zn/Al-Oxalate hydrotalcite, and its characterization results are compared with Zn/Al-NO_3 hydrotalcite to determine the optimum conditions of Zn/Al-Oxalate hydrotalcite in adsorbing methylene blue dye and to determine the kinetic and isotherm models of adsorption. Zn/Al-Oxalate hydrotalcite was successfully synthesized by the coprecipitation method and continued with the hydrothermal process at a temperature of 120°C for 20 hours. Hydrotalcite Zn/Al-Oxalate was characterized using FTIR and XRD. The optimum condition of hydrotalcite Zn/Al-Oxalate in adsorbing methylene blue dye was carried out by the batch method at optimum pH 7, contact time 60 minutes, adsorbent weight 80 mg, and methylene blue concentration 20 mg/L. The adsorption kinetics of hydrotalcite Zn/Al-Oxalate in adsorbing methylene blue followed the pseudo-second-order model. with a value of R^2 = 0.9996 and k = 0.2047 mg/g.min and the adsorption isotherm follows the Langmuir adsorption isotherm model R^2 = 0.9904, q_m = 19.8413 mg/g and k_L = 2.913 L/mg.

1. Introduction

The textile industry is fairly developed in Indonesia. This development is related to the role of textiles as one of the basic human needs besides food and shelter. Development of the textile industry results in increasing waste production, one of which is textile dye waste. It is estimated that 10,000 different types of synthetic dyes and pigments are used for textile industry purposes [1].

Wastewater containing synthetic dyes poses a significant environmental threat due to its potential for accumulation, high toxicity, carcinogenic properties, and resistance to natural degradation [2]. One commonly used dye in the textile industry is methylene blue, valued for its availability and low cost [3]. Methylene blue, with the chemical formula $C_{16}H_{18}ClN_3S$, is a toxic aromatic hydrocarbon compound and cationic dye with strong adsorption capabilities. It is primarily used to dye silk, wool, and textiles [4].

During the dyeing process, only about 5% of methylene blue dye is utilized, while the remaining 95% is discarded as waste. Methylene blue consists of stable aromatic compounds, making textile dye waste difficult to degrade and harmful to the environment, particularly at high concentrations. Additionally, most dyes are designed to resist environmental factors such as pH, temperature, and microbial activity, which leads to an increase in Chemical Oxygen Demand (COD) and disrupts the balance of the ecosystem. This disruption is often evident in the death of aquatic organisms near the waste disposal site [3].

Hydrotalcite is a compound consisting of divalent and trivalent metals, which is a class of clay materials and functions as an effective absorbent [5]. Hydrotalcite can

be synthesized by coprecipitation and hydrothermal methods. Coprecipitation and hydrothermal methods have advantages because the combination of these two methods produces hydrotalcite crystals with larger surface areas, more regular pores, and better thermal stability. In addition, the hydrothermal process can remove impurities and side phases that may form during the coprecipitation process [6].

Hydrotalcite is used as an adsorbent for dye removal from wastewater due to its large surface area, anion exchange capability [7], and regenerability [8]. However, it has the disadvantage of being unable to separate colloidal particles quickly [5]. To enhance the efficiency of dye adsorption, hydrotalcite must be modified through an intercalation process with organic or inorganic anions to increase its surface area [9].

Zn/Al hydrotalcite has higher thermal stability and anion exchange capacity than Mg/Al hydrotalcite [10]. In addition, Zn/Al hydrotalcite has higher adsorption efficiency and capacity and works consistently compared to Mg/Al hydrotalcite [11]. Meanwhile, Zn/Al hydrotalcite intercalated with organic anions forms a better surface area than Zn/Cr hydrotalcite [12].

Based on the description above, in this study, hydrotalcite was modified using divalent metals Zn^{2+} and trivalent Al^{3+}, as well as the addition of oxalate anions. Hydrotalcite was synthesized by coprecipitation and hydrothermal methods, resulting in Zn/Al-Oxalate hydrotalcite. Zn/Al-Oxalate hydrotalcite was applied as an adsorbent for methylene blue dye. The adsorption of methylene blue dye was optimized by varying pH, contact time, adsorbent weight, and dye concentration.

2. Experimental

2.1. Tools and Instruments

The tools used in this study included an analytical balance, magnetic stirrer, oven, Whatman No. 42 filter paper (90 mm diameter), mortar, pH meter, and various glass and plastic support tools. The instruments used were a Shimadzu UV-Vis 1601 Spectrophotometer, Shimadzu XRD-600 X-ray Diffractometer, and Shimadzu FTIR 820 IPC Infrared Spectrophotometer.

2.2. Materials

The materials used in this study were methylene blue (analytical grade, AR), zinc nitrate tetrahydrate ($Zn(NO_3)_2.4H_2O$, AR), aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$, AR), oxalic acid ($C_2H_2O_4$, AR), sodium hydroxide (NaOH, AR), nitric acid (HNO_3, AR), potassium hydroxide (KOH), pH paper, nitrogen gas supplied by PT Samator, distilled water, and double-distilled water.

2.3. Synthesis of Zn/Al-NO_3 Hydrotalcite

A total of 8.9247 g of $Zn(NO_3)_2.4H_2O$ and 3.75 g of $Al(NO_3)_3.9H_2O$ were weighed and dissolved in distilled water to a final volume of 100 mL each. Both solutions were flowed with nitrogen gas for 15 minutes while being stirred with a magnetic stirrer. Subsequently, the solutions were combined to achieve a mole ratio of Zn^{2+} to Al^{3+} of 3:1. The mixture was continuously stirred with a magnetic stirrer and purged with nitrogen gas for 30 minutes.

Next, 0.5 M NaOH was added dropwise to adjust the pH to 10. Stirring was continued for 2 hours, and nitrogen gas was maintained to minimize carbonate ions that could affect the purity of hydrotalcite. The resulting slurry was subjected to hydrothermal treatment at 120°C for 20 hours. The hydrothermal product was centrifuged at 2500 rpm for 15 minutes. The supernatant was discarded, and the residue was filtered and washed with double-distilled water using Whatman No. 42 filter paper. The precipitate obtained was dried in an oven at 120°C for 5 hours. The synthesized material, designated as Zn/Al- NO_3, was then characterized using FTIR and XRD [13].

2.4. Synthesis of Zn/Al-Oxalate Hydrotalcite

A total of 8.9247 g of $Zn(NO_3)_2.4H_2O$ and 3.75 g of $Al(NO_3)_3.9H_2O$ were weighed and dissolved in distilled water to prepare separate solutions, each with a final volume of 100 mL. Both solutions were flowed with nitrogen gas for 15 minutes while being stirred with a magnetic stirrer. The solutions were then combined to achieve a mole ratio of Zn^{2+} to Al^{3+} of 3:1, with continuous stirring and nitrogen gas purging for 30 minutes. Subsequently, 100 mL of 0.7 M $C_2H_2O_4$ solution was added, followed by the dropwise addition of 0.5 M NaOH until the pH reached 10. The mixture was stirred for 2 hours, and nitrogen gas was passed through to minimize carbonate ions that could affect the purity of hydrotalcite. The resulting slurry was subjected to hydrothermal treatment at 120°C for 20 hours.

After hydrothermalization, the product was centrifuged at 2500 rpm for 15 minutes. The residue was filtered and washed with double-distilled water using Whatman No. 42 filter paper. The precipitate obtained was dried in an oven at 120°C for 5 hours. The synthesized material, referred to as Zn/Al-Oxalate, was then characterized using FTIR and XRD [13].

2.5. Determination of Calibration Curve

A calibration curve was made using standard solutions of methylene blue dye at concentrations of 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 ppm. These standard solutions were prepared by diluting a 100 mg/L stock solution of methylene blue to the desired concentrations in 10 mL volumetric flasks. The standard solutions were analyzed using a UV-Vis spectrophotometer at a wavelength of 664 nm [14].

2.6. Methylene Blue Adsorption Study

2.6.1. Effect of pH

The adsorption process was carried out using the batch method. A total of 10 mg of hydrotalcite was added to 16 mL of 4 mg/L methylene blue solution with a pH variation of 2-11 [15]. The mixture was then homogenized using a shaker for 1 hour. The solution was separated from the adsorbent by centrifugation at a speed of 4000 rpm; then, the methylene blue content was analyzed using a UV-Vis spectrophotometer.

2.6.2. The Influence of Time

The adsorption process was carried out using the batch method. A total of 10 mg of hydrotalcite was added to 16 mL of 4 mg/L methylene blue solution at optimum pH. The mixture was then homogenized using a shaker with a time variation of 1-2 hours [15]. The solution was separated from the adsorbent by centrifugation at a speed of 4000 rpm, and then the methylene blue content was analyzed using a UV-Vis spectrophotometer.

2.6.3. Effect of Adsorbent Weight

The adsorption process was carried out using the batch method. A total of 16 mL of 4 mg/L methylene blue solution was added with hydrotalcite with a weight variation of 5-100 mg at optimum pH. The mixture was then homogenized using a shaker at the optimum time. The solution was separated from the adsorbent by centrifugation at a speed of 4000 rpm, and then the methylene blue content was analyzed using a UV-Vis spectrophotometer.

2.6.4. Effect of Methylene Blue Concentration

The adsorption process was carried out using the batch method. Hydrotalcite at optimum weight was added to 16 mL of methylene blue solution with a concentration variation of 10-100 mg/L at optimum pH. The mixture was then homogenized using a shaker at optimum contact time. Furthermore, the solution was separated from the adsorbent by centrifugation at a speed of 4000 rpm, and the methylene blue content was then analyzed using a UV-Vis spectrophotometer.

2.7. Determination of Adsorption Kinetics

The data from the adsorption study on determining the optimum contact time were used to determine the kinetics of the adsorption reaction using the first-order, second-order, pseudo-first-order Lagergren, and pseudo-second-order Ho equations. The first-order and second-order reaction kinetic models were calculated using the ln C_0/C_e graph against t and $(1/C_e)$ against t, respectively. The values of q_e and k_1 in the pseudo-first-order Lagergren can be determined by making a linear regression equation between log (q_e - q_t) vs t. Meanwhile, the values of q_e and k_2 in the pseudo-second-order Ho can be determined using a linear regression equation between t/q_t and t.

2.8. Determination of Adsorption Isotherms

The adsorption data were analyzed to identify the optimum concentration and the corresponding adsorption isotherm model. The Langmuir isotherm was evaluated using its specific equation, while the Freundlich isotherm was assessed using its respective equation. Similarly, the Temkin isotherm was examined using its equation, and the Harkin-Jura isotherm was analyzed using its equation. The selection of the most suitable isotherm model was based on the regression coefficient (R^2) being close to 1 and the evaluation of error functions. The model with the smallest error was considered the best fit for describing the adsorption behavior.

2.9. Determination of Percentage Reduction in Methylene Blue Concentration

The percentage of decrease in methylene blue dye concentration was determined using a calibration curve to determine the concentration of the absorbance value obtained. The concentration value of the solution obtained was used to determine the percentage of decrease in methylene blue dye concentration using Equation (1) [16].

$$Concentration\ decrease\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

3. Results and Discussion

3.1. Synthesis of Zn/Al-NO_3 Hydrotalcite

Zn/Al-NO_3 hydrotalcite was successfully synthesized using coprecipitation and hydrothermal methods. The 3:1 ratio of Zn^{2+} to Al^{3+} ensures charge balance, resulting in a stable and orderly hydrotalcite structure, as the differing ionic sizes also influence its formation [13]. During coprecipitation, nitrogen gas is introduced to prevent CO_2 contamination, as atmospheric CO_2 can react with water to form carbonate ions (CO_3^{2-}), which may occupy interlayer spaces intended for NO_3^- ions. Carbonate ions form larger and stronger bonds than many other anions, potentially altering the desired structure.

As a result, carbonate ions can change the spacing between hydrotalcite layers, affecting its ability to adsorb other ions and allowing the hydrotalcite crystal shape to change. Carbonate ions can cover part of the hydrotalcite surface, reducing the surface area available for chemical reactions. This can reduce the ability of hydrotalcite as a catalyst or adsorbent [17]. The reaction equation is shown in Equations (2) to (4) [18].

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (2)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (3)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad (4)$$

Nitrogen gas flowing in the right amount can push and remove carbonate ions, which are then released as CO_2. The reaction equation that occurs is shown in Equations (5) and (6).

$$N_2 + 2H_2O \rightarrow 2NO^{2-} + 4H^+ \quad (5)$$

$$2CO_3^{2-} + 4H^+ \rightarrow 2H_2O + 2CO_2 \quad (6)$$

The synthesized Zn/Al-NO_3 hydroxide appears white and is formed according to Equation (7).

$$3Zn(NO_3)_{2(aq)} + Al(NO_3)_{3(aq)} + 8NaOH_{(aq)} \rightarrow Zn_3Al(OH)_8(NO_3)_{(s)} + 8NaNO_{3(aq)} \quad (7)$$

3.2. Synthesis of Zn/Al-Oxalate Hydrotalcite

Zn/Al-Oxalate hydrotalcite was synthesized using coprecipitation and hydrothermal methods. The addition of oxalate anions facilitates the intercalation process, replacing the initial anion (NO_3^-, nitrate) with $C_2O_4^{2-}$ (oxalate), thereby increasing the interlayer spacing of the hydrotalcite structure. The synthesized Zn/Al-Oxalate hydrotalcite appears as a white powder, as described by Equations (8) and (9).

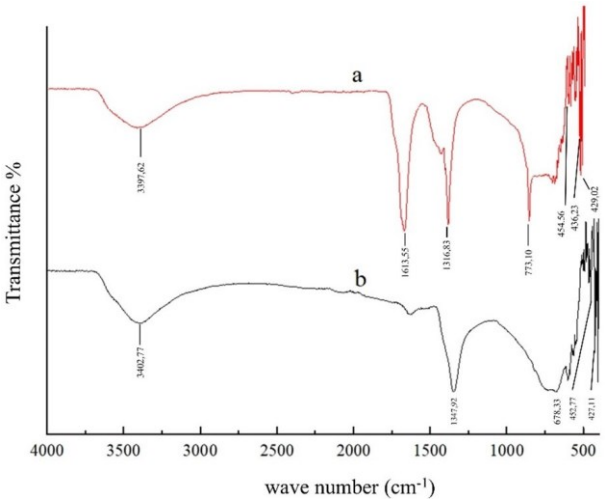

Figure 1. FTIR spectra of (a) Zn/Al-Oxalate hydrotalcite and (b) Zn/Al-NO_3 hydrotalcite

$$3Zn(NO_3)_{2(aq)} + AI(NO_3)_{3(aq)} + 8NaOH_{(aq)} \rightarrow Zn_3Al(OH)_8(NO_3)_{(s)} + 8NaNO_{3(aq)} \quad (8)$$

$$Zn_3Al(OH)_8(NO_3)_{(aq)} + C_2H_2O_{4(aq)} \rightarrow Zn_3Al(OH)_7C_2O_{4(s)} + HNO_{3(aq)} + H_2O_{(aq)} \quad (9)$$

3.3. Characterization of Zn/Al-NO_3 Hydrotalcite and Zn/Al-Oxalate Hydrotalcite

3.3.1. FTIR Characterization

FTIR characterization of Zn/Al-NO_3 hydrotalcite and Zn/Al-Oxalate hydrotalcite was conducted to analyze the molecular structure of the compounds by identifying their functional groups. The FTIR characterization results are presented in Figure 1. The FTIR spectrum of Zn/Al-NO_3 hydrotalcite shows an absorption band at 3402.77 cm^{-1}, indicating the presence of OH functional groups. Absorption at 1347.92 cm^{-1} corresponds to the N=O functional group, while bands at 452.77 cm^{-1} and 427.11 cm^{-1} represent Al–O, and Zn–O–Al functional groups, respectively. For Zn/Al-Oxalate hydrotalcite, absorption appears at 3397.62 cm^{-1}, signifying the OH functional group, and at 1613.55 cm^{-1}, corresponding to the C=O functional group.

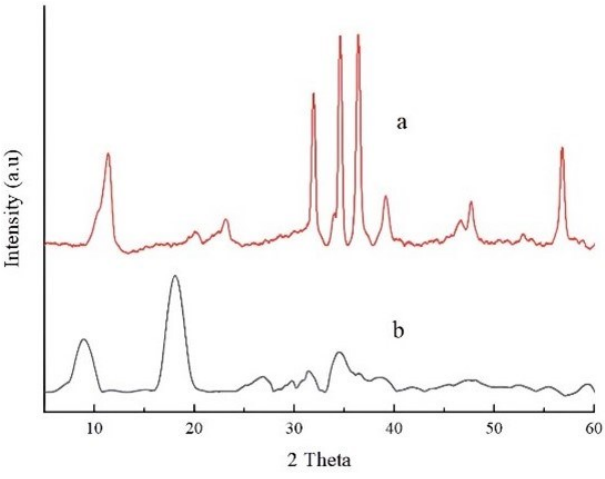

Figure 2. XRD spectra of (a) Zn/Al-Oxalate hydrotalcite and (b) Zn/Al-NO_3 hydrotalcite

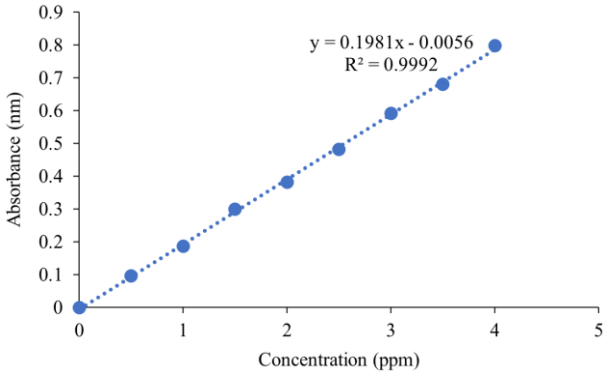

Figure 3. Calibration curve of methylene blue standard solution

The FTIR spectrum reveals additional absorption bands at 1316.83 cm^{-1}, corresponding to the N=O functional group, 454.56 cm^{-1} for the Al–O functional group, and 429.02 cm^{-1} for the Zn–O–Al functional group, which are characteristic of the hydrotalcite structure. In the Zn/Al-Oxalate hydrotalcite, distinct vibrations at 1385 cm^{-1} and 1261 cm^{-1} confirm the presence of C–O bonds from oxalate anions, indicating the successful incorporation of oxalate into the interlayer spaces. A significant reduction in the nitrate peak intensity suggests an effective ion exchange process, where oxalate ions replace nitrate ions within the Zn/Al-$(COO)_2^{2-}$ structure, demonstrating a complete exchange [9]. Based on Figure 1, these results confirm the successful synthesis of Zn/Al-NO_3 hydrotalcite and Zn/Al-Oxalate hydrotalcite in this study.

C–O bonds in Zn/Al hydrotalcite originate from the carboxylate group (COO^-) of the oxalate ion, which has been successfully intercalated between the hydrotalcite layers. Strong C–O bonds between the oxalate ions and the hydrotalcite layers contribute to enhanced structural stability due to the formation of robust interactions within the layers. Incorporating oxalate ions, larger than nitrate ions, increases the interlayer spacing within the hydrotalcite structure. This change can influence the material's physical and chemical properties, including its adsorption capacity. Both oxalate and nitrate ions possess sizes and charges that enable them to occupy interlayer positions in the hydrotalcite structure [19].

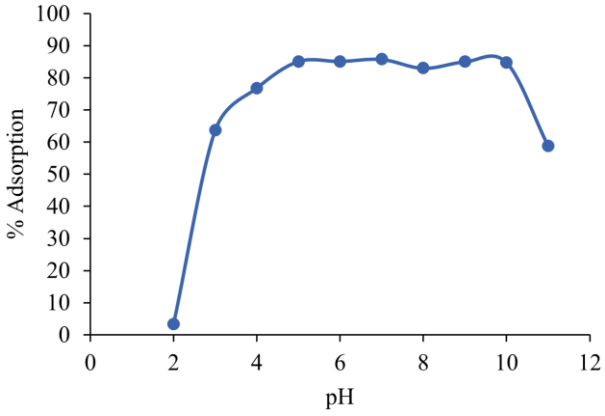

Figure 4. Effect of pH on the percentage of methylene blue adsorption

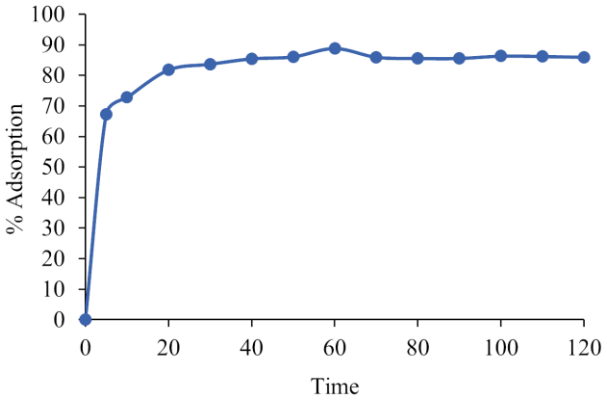

Figure 5. Effect of contact time on the percentage of methylene blue adsorption

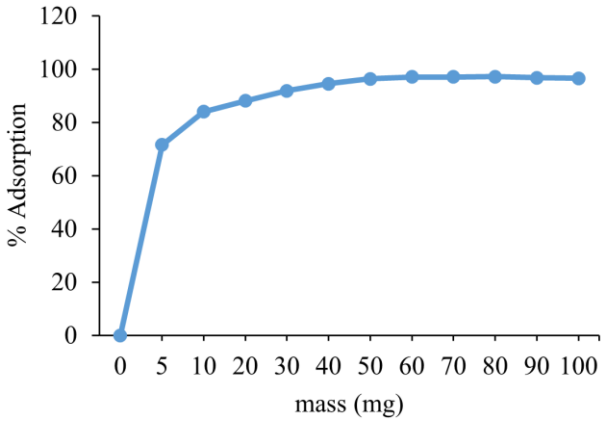

Figure 6. Effect of Zn/Al-Oxalate hydrotalcite weight on the percentage of methylene blue adsorption

3.3.2. XRD Characterization

XRD is a basic characterization to determine the phase and size of the crystal. The material to be characterized by XRD must be in a solid phase because in this state, the position of the atoms is arranged regularly and forms crystal planes so that when shot by X-rays, a diffraction pattern will appear [20]. The results of the XRD characterization are shown in Figure 2.

The XRD analysis of Zn/Al-Oxalate hydrotalcite revealed peaks at 2θ positions of 9.1303°, 18.0511°, 29.4529°, 31.6972°, 34.5125°, 38.6496°, and 55.4692°. In contrast, Zn/Al-NO_3 hydrotalcite showed peaks at 2θ positions of 11.3781°, 20.0070°, 31.8806°, 34.5222°, 36.3591°, 39.0486°, and 56.7590°. The crystal diameter of Zn/Al-Oxalate hydrotalcite was determined to be 29.90 nm, larger than that of Zn/Al-NO_3 hydrotalcite, which measured 25.93 nm. These results suggest that the intercalation of oxalate ions expands the interlayer spacing, leading to a larger crystal diameter. This structural modification likely enhances the adsorption capacity of Zn/Al-Oxalate hydrotalcite compared to Zn/Al-NO_3 hydrotalcite [11].

3.4. Methylene Blue Calibration Curve

A calibration curve is a graph that illustrates the relationship between the response of the measuring instrument and various known concentration levels of the material being analyzed [21]. A series of standard solutions were analyzed using a UV-Vis spectrophotometer at a maximum wavelength of 664 nm [14]. The resulting calibration curve yielded an R^2 value of 0.9992, with the linear equation y = 0.1981x – 0.0056 (Figure 3).

3.5. Methylene Blue Adsorption Study

3.5.1. Effect of pH

The pH value plays an important role in the adsorption process and affects the adsorption capacity and the ability of the adsorbent surface to absorb dyes. The adsorption capacity is closely related to the pH of the solution because changes in pH result in variations in the degree of ionization of the dye and the type of dominant charge on the adsorbent surface. The presence of hydroxyl ions (OH^-) and hydrogen ions (H^+) used in pH adjustments play a role in influencing the interaction between the adsorbent and the adsorbate molecules [22]. This study produced the optimum pH of Zn/Al-Oxalate hydrotalcite in adsorbing methylene blue dye solution at pH 7 with an adsorption percentage of 85.79% (Figure 4).

3.5.2. The Influence of Time

The adsorption study of the effect of contact time was carried out using the batch method. The longer the contact time of Zn/Al-Oxalate hydrotalcite to methylene blue dye, the greater the percentage of adsorption obtained. Figure 5 shows that the reaction reaches equilibrium at 60 minutes with an adsorption percentage of 88.82%.

3.5.3. Effect of Adsorbent Weight

The effect of Zn/Al-Oxalate hydrotalcite adsorbent weight was investigated in the range of 5-100 mg. The optimum adsorbent weight was found to be 80 mg, which resulted in an adsorption percentage of 97.15%. However, when the adsorbent weight was increased to 90 mg and 100 mg, the adsorption percentage decreased to 96.77% and 96.52%, respectively (Figure 6). As the adsorbent weight increases, more surface area becomes available for the adsorbate until the hydrotalcite reaches saturation in adsorbate binding. Additionally, the higher adsorbent weight leads to an increase in the number of oxalate ions, enhancing the complexation between the adsorbate and the adsorbent, thereby improving the adsorption percentage [23].

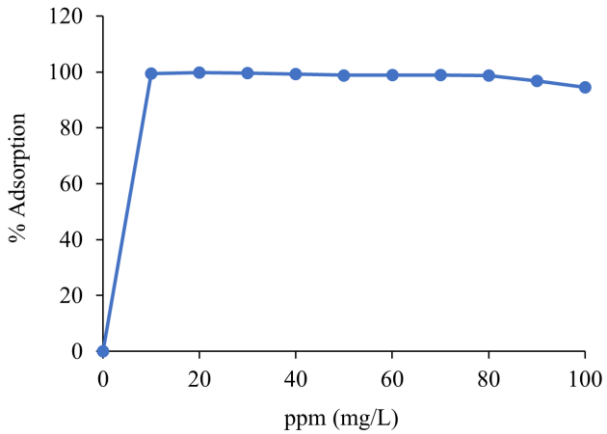

Figure 7. Effect of methylene blue concentration on the adsorption percentage of methylene blue

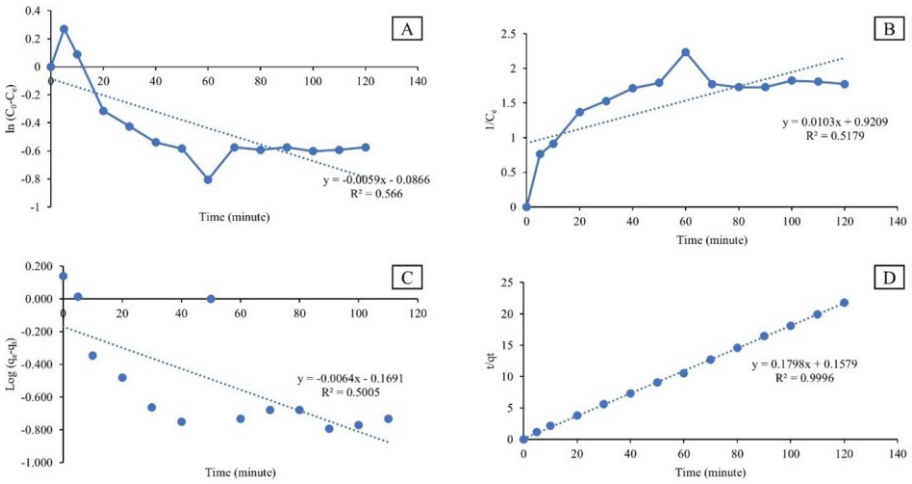

Figure 8. Adsorption kinetics of methylene blue: (A) First-order, (B) Second-order, (C) Pseudo-first-order Lagergren, and (D) Pseudo-second-order Ho models

3.5.4. Effect of Methylene Blue Concentration

The concentration effect is crucial in determining the maximum adsorption capacity of an adsorbent. The relationship between the initial dye concentration and the adsorption capacity is key for selecting the appropriate adsorption isotherm model [22]. The optimum concentration was 20 ppm, resulting in an adsorption percentage of 99.56% and a q_e value of 17.425 mg/g (Figure 7).

3.6. Adsorption Kinetics

The kinetics of methylene blue dye adsorption in this study were analyzed using data obtained from the effect of the optimum contact time. The adsorption data were fitted to the first-order, second-order, pseudo-first-order Lagergren, and pseudo-second-order Ho reaction models. From the first-order and second-order equations, the slope and R^2 values were determined, while the pseudo-first-order Lagergren and pseudo-second-order Ho equations provided the values for k, q_e, and R^2.

Figure 8 shows that the adsorption kinetics of methylene blue dye using Zn/Al-Oxalate hydrotalcite follows the pseudo-second-order Ho kinetic model. This is evidenced by the correlation coefficient (R^2) of 0.9996, the highest value and closest to 1 (Table 1). The R^2 value indicates that the adsorption capacity is proportional to the number of active sites in the adsorbent [24]. Additionally, the adsorption rate constant (k) obtained from the pseudo-second-order Ho model is 0.2047 mg/g·min, meaning that 1 mg of adsorbent can adsorb 0.2047 mg of adsorbate per minute. A higher adsorption rate constant suggests a faster adsorption process [25].

3.7. Adsorption Isotherm

The adsorption process by an adsorbent is influenced by several factors, such as the type of adsorbent, the type of substance absorbed, the surface area of the adsorbent, the concentration of the substance adsorbed, and the temperature [26]. Solid-liquid phase adsorption usually follows the Langmuir isotherm and Freundlich isotherm types. However, in this study, the adsorption isotherm was also carried out using the Temkin and Harkin-Jura isotherm models.

Based on Figure 9, the Langmuir adsorption isotherm model is the most appropriate for this study, as it has the highest correlation coefficient (R^2) value of 0.9904, which is closest to 1 compared to the other models (Table 2). The Langmuir isotherm model suggests that the adsorption process occurs in a single layer on a homogeneous surface [15].

The qm value in the Langmuir adsorption isotherm represents the maximum adsorption capacity of 19.8413 mg/g. The Langmuir constant (kL) is 2.913 L/mg, indicating the equilibrium constant for the isotherm adsorption. A higher kL value corresponds to a greater adsorption capacity.

Table 1. Adsorption kinetics of Zn/Al-Oxalate hydrotalcite for methylene blue

Kinetic Model	Equality	R^2	k
First order	y = -0.0059x - 0.0866	0.566	-0.0059 minutes^{-1}
Second order	y = 0.0103x + 0.9209	0.5179	0.0103 minutes^{-1}
Pseudo first order	y = -0.0064x - 0.1691	0.5005	0.0147 mg/g.min
Pseudo second order	y = 0.1798x + 0.1579	0.9996	0.2047 mg/g.min

Table 2. Comparison of Langmuir, Freundlich, Temkin, and Harkin-Jura adsorption isotherms

Isotherm	R^2	Parameter 1	Parameter 2	Energy (J/mol)
Langmuir	0.9904	q_m (mg/g) 19.8413	k_L (L/mg) 2.913	19,763.5918
Freundlich	0.3108	n 2.8098	k_F (mg/g) 9.3197	5,530.1885
Temkin	0.565	b_T (J/mol) 14,101.1497	k_T (L/g) 1.1561×10^{-6}	33,869.6480
Harkin-Jura	0.4374	A (mg/g) 13.1926	B (mg/g) 0.1728	-

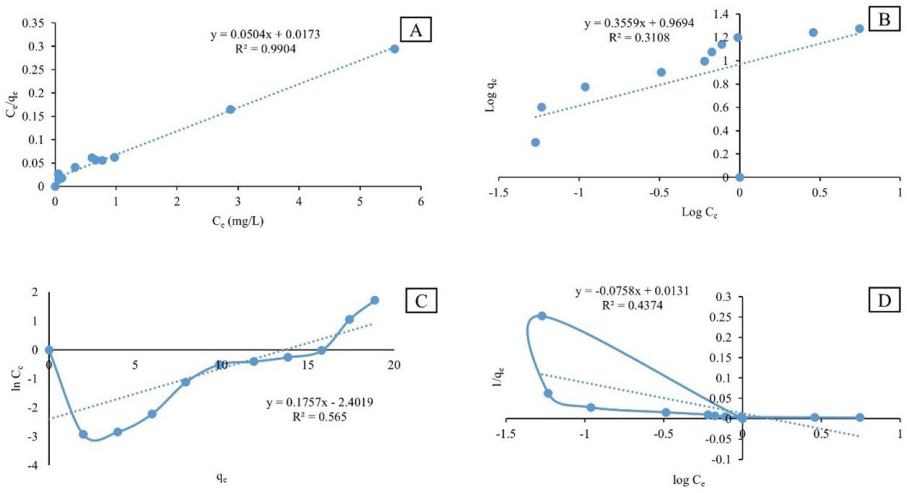

Figure 9. Adsorption isotherms of methylene blue: (A) Langmuir, (B) Freundlich, (C) Temkin, and (D) Harkin-Jura

3.8. Percentage Reduction of Methylene Blue Concentration

The data on the effect of methylene blue concentration were used to determine the percentage decrease in methylene blue concentration. This percentage reflects the reduction in the initial concentration of methylene blue before adding the Zn/Al-Oxalate hydrotalcite adsorbent, compared to the final concentration after the adsorbent's addition. The results show that Zn/Al-Oxalate hydrotalcite successfully adsorbed 99.71% of the methylene blue solution, demonstrating its high efficacy in adsorbing methylene blue under optimal conditions of pH, time, adsorbent weight, and concentration.

4. Conclusion

The synthesis of Zn/Al-Oxalate hydrotalcite was successfully performed using the coprecipitation method, followed by hydrothermal treatment at 120°C for 20 hours. The resulting Zn/Al-Oxalate hydrotalcite was white in color. Characterization using FTIR and XRD confirmed the replacement of the nitrate anion by the oxalate anion. The adsorption kinetics of methylene blue dye followed the pseudo-second-order model with R^2 = 0.9996 and k = 0.2047 mg/g.min, while the adsorption isotherm adhered to the Langmuir model with R^2 = 0.9904, q_m = 19.8413 mg/g, and kL = 2.913 L/mg. These findings indicate that Zn/Al-Oxalate hydrotalcite adsorbs methylene blue dye in a monolayer via chemisorption.

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