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Composite Layered Double Hydroxide Zn-Al/Magnetic Biochar Modified for Highly Effective Malachite Green Adsorption

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ABSTRACT

One of the main needs of humans is water, one source of water pollutantion is from dyes. Adsorption is the most popular method in removing pollutants as it is proven to be efficient. One of the dyes harmful to living things is malachite green. In this study, malachite green dye was removed using a layered double hydroxide (LDH) Zn-Al/magnetic biochar composite. The XRD, FTIR, BET, and VSM analyses show that the LDH Zn-Al, magnetic biochar, and LDH Zn-Al/magnetic biochar composite were successfully produced. The surface area of the Zn-Al/magnetic biochar composite made up of LDH increased from 9.621 m^2/g to 99.473 m^2/g. The point of zero charge of LDH Zn-Al and magnetic biochar were at pH 6, whereas the composite of these two materials was at pH 7. For LDH Zn-Al, magnetic biochar, and composite LDH Zn-Al/magnetic biochar, pH 8 is the ideal value for adsorption of malachite green. PSO (pseudo-second order) kinetics is the best-fit model. LDH Zn-Al, magnetic biochar, and LDH Zn-Al/magnetic biochar composite had adsorption capacities of 14.472, 15.552, and 25.907 mg/g, respectively, at a temperature of 60°C. Regeneration showed the LDH Zn-Al/magnetic biochar composite had superior and more effective ability compared to LDH Zn-Al and magnetic biochar.

1. INTRODUCTION

One of the main human needs is water. Rivers are one of the water sources used for daily human life. Therefore, river water must be clean from pollutants. One source of pollutants is dyes from the textile industry (Mahmoodi et al., 2018; Mokhtari-Shourijeh et al., 2020; Hosseinabadi-Farahani et al., 2015). The textile industry uses about 10,000 color pigments. Dye is lost during the drying process, and as much as 1-15% of the dye is released into wastewater (Lv et al., 2022). Dye effluent contains suspended particles and a high pH, and dyes are also hazardous to health because they have carcinogenic, genotoxic, mutagenic, and teratogenic properties (Hasanah et al., 2022; Yan et al., 2022; Mahmoodi et al., 2017). These problems can cause negative effects on the environment and health so ways are needed to overcome them. Many methods can be used to overcome liquid waste, especially dyes, such as precipitation, chemical degradation, photo-degradation, biodegradation, coagulation, and adsorption (Dai et al., 2022; Faggio et al., 2022; Li et al., 2022; Selvanathan et al., 2017; Mahmoodi and Mokhtari-Shourijeh, 2016; Mahmoodi et al., 2017). Among these methods, adsorption is the most popular method as it is proven to be efficient in removing pollutants from effluents (Palapa et al., 2020; dos Santos et al., 2021).

Adsorption is the most widely used technique for pollutant removal. This is due to its efficiency in removing very low amounts of contaminants from aqueous solutions, speed, cost-effectiveness,

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universality among numerous water treatment systems, ease of handling, excellent selectivity, and adsorbent regeneration (Badhai et al., 2020; Ho and Adnan, 2021; Liao et al., 2022; Rabeie and Mahmoodi, 2024). Layered double hydroxide is one of the materials that can be utilized in the adsorption method to purify water. This substance has been developed considerably because it is distinct and has good absorption. Due to its low cost and substantial surface area, it has a lot of potential for use as an adsorbent in the treatment of water (Bouteraa et al., 2020; Cheng et al., 2022; Zubair et al., 2022). According to Vithanage et al. (2020), stacked double hydroxide can be utilized as an adsorbent to remove organic and inorganic species, colors, and hazardous metal pollutants from water. Rathee et al. (2019) reported that layered double hydroxide applied as an adsorbent has limitations in the regeneration process. According to Normah et al. (2021) and Yuliasari et al. (2022), LDH tends to have unstable adsorption effectiveness due to damage to the layer structure during the application process. To create a composite, layered double hydroxide must be changed with supporting elements made of carbon. Composites are materials formed through the combination of two or more different materials and become one material microscopically where the forming material is still visible and does not change the properties of each material (Lee et al., 2019).

According to the research of Wijaya et al. (2021) malachite green was adsorbed using composite layered double hydroxide Cu-Al/carbon with an adsorption capacity of 49.505 mg/g. Congo red was adsorbed using layered double hydroxide Ni-Al with an adsorption capacity of 61.728 mg/g (Siregar et al., 2021). Research Mohadi et al. (2021) reported a malachite green dye using LDH Ca/Al had a maximum adsorption capacity of 43.860 mg/g, while Ca/Al which had been composited with biochar has an increase in maximum adsorption capacity to 71.429 mg/g. Layered double hydroxide CuAl and CuAl/biochar composites adsorb malachite green dye at an optimum pH of 9 with adsorption capacities of 20 mg/g and 25 mg/g, respectively (Palapa et al., 2020). Layered double hydroxide modified using carbon to improve performance stability in adsorbing dyes can also be used repeatedly (Palapa et al., 2019).

Zn-Al layered double hydroxide magnetic composites have been carried out by Ahmad et al. (2023) to adsorb congo red dye and produced better regeneration than using pristine layered double hydroxide. Making magnetic composites by combining layered double hydroxide with activated carbon, can combine the advantages of both types of materials, such as high adsorption capacity and good separation efficiency (Ahmad et al., 2023). Some of the advantages of using magnetic layered double hydroxide composite materials are efficient separation, efficient regeneration, and targeted control to direct adsorbents to specific areas using magnetic fields improves control over the adsorption process, especially in the case of dye removal. In addition, the use of magnetic materials can simplify the separation and adsorption process, reducing operational complexity. As for the disadvantage of using these materials, namely production costs, magnetic materials are often more expensive to produce compared to conventional adsorbents, and this can be an obstacle to their application. The selection of suitable magnetic materials that have good adsorption properties for certain dyes is a key factor in the success of adsorption (Ahmad et al., 2023). The first regeneration of a Zn-Al layered double hydroxide magnetic composite recovered up to 100% activity compared to Zn-Al layered double hydroxide at only 76.99% (Ahmad et al., 2023). In this study, LDH Zn-Al was composited with biochar magnets which were then characterized using XRD, FT-IR, BET, and VSM. Malachite green dye's ability to bind to different materials was determined by evaluating factors like pH, pHpzc, time, concentration, temperature, and material regeneration.

2. METHODOLOGY

2.1 Chemicals and instrumentation

Materials and tools used are zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$, aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) (Sigma-Aldrich, 375.13 g/mol), sulfuric acid (H_2SO_4), graphite, sodium hydroxide (NaOH) (EMSURE® ACS, 40 g/mol), sodium carbonate (Na_2CO_3) (EMSURE® ACS, 105.99 g/mol), sodium nitrate ($NaNO_3$), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), ammonia (NH_3), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl) (MallinckrodtAR®, 37%), distilled water (H_2O), biochar, malachite green ($C_{23}N_2H_{25}Cl$). The tools used were a magnetic stir bar, separatory funnel, hotplate, filter paper, analytical balance, oven, pH meter, shaker, standard glassware including Erlenmeyer, beaker, measuring cup, drip pipettes, and volumetric pipettes, analysis XRD Rigaku Miniflex-6000, Spectrophotometer FT-IR Shimadzu Prestige-21, BET equipment Quantachrome Instruments, Spectrophotometer UV-Vis Biobase BK- UV 1800 PC, and VSM250-P2F.

2.2 Synthesis of Zn-Al LDH

Zn-Al layered double hydroxide synthesis was carried out with 100 mL of 0.75 M $Zn(NO_3)_2{\cdot}6H_2O$ mixed with 100 mL of 0.25 M $Al(NO_3)_3{\cdot}9H_2O$, then dripped into 50 mL of 2 M NaOH solution. NaOH was used to get the mixture's pH to 10, after which it was agitated for four hours at 80°C (Rahmadan et al., 2021; Palapa et al., 2019). The precipitate was stirred, then filtered and washed with distilled water to get rid of any contaminants. XRD analysis, FTIR spectrophotometer, BET, and VSM was utilized to characterize the solid produced after the precipitate was oven-dried.

2.3 Preparation of magnetic biochar

To make magnetic biochar, as much as 1 g of $FeCl_3$ dissolved in 3 mL of distilled water was mixed with 0.6 g of $FeSO_4{\cdot}7H_2O$ dissolved in 3 mL of distilled water. One gram of biochar was added to the mixed solution and then stirred for three hours. The mixture formed was slowly dripped with 3.5 mL NH_3 solution and then stirred for 30 min at 75°C. The solution formed was put into a 100 mL hydrothermal stainless steel autoclave. After that, the mixture was then heated for three hours at 150°C. Magnetite biochar solid product was filtered and dried at 40°C. Magnetite biochar solids were characterized using XRD, FT-IR, BET, and VSM tools (Ahmad et al., 2023; Cheng et al., 2022).

2.4 Preparation of composite magnetic biochar-modified layered double hydroxide Zn-Al

Fifteen mL each of 0.75 M Zn and 0.25 M Al solutions were combined, and the pH was then brought to 10 by adding 15 mL of NaOH solution. Three grams of biochar was then added after the mixture had been agitated for an hour to become homogenous and form a gel. $FeCl_3$ was added in the amount of 2 g, dissolved in 3 mL of distilled water, together with 1.6 g of $FeSO_4{\cdot}7H_2O$, and agitated for three hours at room temperature to create solution A. For 72 h, the solution was kept at 80°C. The mixture formed was slowly dripped with 7 mL NH_3 solution and stirred at 75°C for 30 min so that solution B was formed. Thirty minutes of stirring followed by adding solution B to solution A. The created solution was heated at 150°C for 72 h in a 100 mL hydrothermal stainless autoclave. The solid obtained was filtered washed with distilled water and dried in the oven at 100°C for 24 h. The dried Zn-Al/magnetite biochar composite was crushed and analyzed by XRD, FT-IR, BET, and VSM (Ahmad et al., 2023; Cheng et al., 2022; Siregar et al., 2021; Dai et al., 2022).

2.5 Performance of pH optimum

A total of 20 mL of dye at a concentration of 45 mg/L was put into a 100 mL beaker and the pH adjusted using NaOH and HCl solutions with pH variations of 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11. Then the initial absorbance of each solution was measured using a UV-Vis spectrophotometer to determine the initial concentration at various pHs. A total of 0.02 g of materials was added to the malachite green dye selective solution and stirred for two hours. Centrifugation was used for the separation procedure, and a UV-Vis spectrophotometer was used to measure the filtrate (Wijaya et al., 2021; Normah et al., 2021; Lesbani et al., 2020).

2.6 Performance of pH point zero charges (pHpzc)

LDH Zn-Al, biochar, composite layered double hydroxide Zn-Al/Biochar, and magnetic Zn-Al/Biochar, were added in amounts of up to 0.02 g to 20 mL of a 0.1 M NaCl solutions that had been adjusted to pH values of 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11. NaOH and HCl solutions with a concentration of 0.1 M were added to the NaCl solution to change the pH. A pH meter was used to test the final pH of the mixture after it had been agitated for 24 h. The correlation between the initial and final pHs was then plotted on a graph (Hasanah et al., 2022; Rathee et al., 2019; Siregar et al., 2022).

2.7 Adsorption of color substances

The adsorption process was carried out by adding 0.02 g of adsorbent to as much as 20 mL of a 60 mg/L malachite green dye solution, then stirring with adsorption contact times of 0, 5, 10, 15, 20, 30, 60, 90, 100, 120, 150, and 180 min. In the variation of concentration and temperature, concentrations of 60 mg/L, 70 mg/L, 80 mg/L, 90 mg/L, and 100 mg/L with temperature variations of 30°C, 40°C, 50°C, and 60°C were used (Zubair et al., 2022; Yuliasari et al., 2022; Liao et al., 2022). The solutions were stirred for two hours. After the stirring was complete, the adsorbent was separated from each dye solution using centrifugation. The separated solution was measured for absorbance value using a UV-Vis spectrophotometer.

2.8 Regeneration

By introducing adsorbents that have undergone the desorption process an ultrasonic instrument, the regeneration process is carried out. First, 1 g of adsorbent was added to 20 mL of a 50 mg/L solution of malachite green dye. Next, the mixture was agitated for two hours. The adsorbent that had been used was dried. After drying, 0.2 g of the residue was added to 10 mL of water solvent and desorbed for two hours using an ultrasonic device. The next regeneration process was carried out by mixing 0.2 g of desorbed adsorbent with as much as 20 mL of 50 mg/L of dye solution. The mixture was stirred for two hours and the residual concentration was measured using a UV-Vis spectrophotometer. The adsorbent then underwent the next regeneration (Mohadi et al., 2021; Palapa et al., 2020).

3. RESULTS AND DISCUSSION

3.1 Point of zero charge (PZC) of the adsorbent materials

In determining the state of zero-charged material on LDH Zn-Al, magnetic biochar, and LDH ZnAl/magnetic biochar composites, the pH pzc method was used. The pH pzc measurement was done by making 15 mL of a 0.1 M NaCl solution as and then adding 0.015 g of ZnAl layered double hydroxide material, magnetic biochar, or ZnAl/magnetic biochar layered double hydroxide composite. Then, the pH condition was adjusted by adding 0.1 M HCl and 0.1 M NaOH, and the solution was shaken for 24 h. Then, filtrates were taken and a pH meter recorded final pH from each material.

Figure 1 shows the state of the pH pzc graphs of ZnAl layered double hydroxide material, magnetic biochar, and ZnAl/magnetic biochar layered double hydroxide composite. The line intersection at pH pzc of layered double hydroxide ZnAl and magnetic biochar is seen at pH 6 and pH pzc of layered double hydroxide ZnAl/magnetic biochar composite is pH 7. At pH conditions from pH 6-7 for layered double hydroxide ZnAl and magnetic biochar materials, and layered double hydroxide ZnAl/magnetic biochar composite shows that pH > pH pzc. At pH < pH pzc, this indicates a positive charge on the adsorbent surface, so this can increase the adsorption capacity due to the attractive force between the positive charge of the adsorbent and the negative charge on the dye (Ahmad et al., 2023). Based on the research by Amri and Hanifah (2023) on the adsorption of malachite green using graphene oxide, the optimum pH > pHpzc on graphene oxide material. This suggests that the graphene oxide surface has a large number of negative charges. Due to the difference in charge between graphene oxide and the positively charged malachite green dye, there is an electrostatic interaction between the two materials.

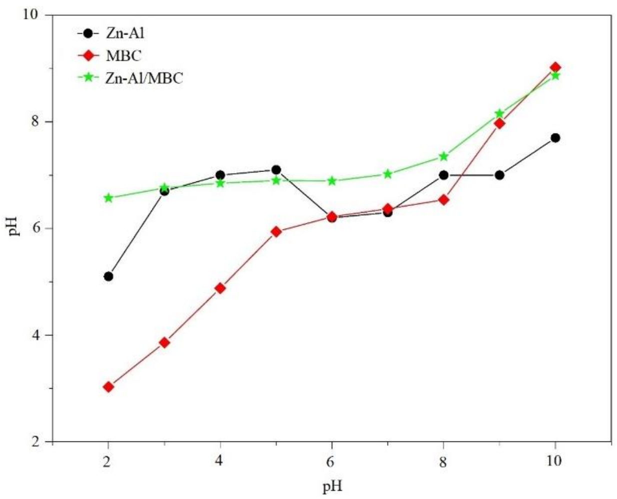

Figure 1. Pzc of adsorbent materials

3.2 Effect of pH

The effect of pH variation on the adsorption of malachite green on LDH adsorbent Zn-Al, magnetic biochar, and LDH composite Zn-Al / magnetic biochar is presented in Figure 2. Figure 2 shows an increase in the adsorbed concentration of LDH adsorbent Zn-Al, magnetic biochar, and LDH composite Zn-Al/ magnetic biochar. Figure 2 graph shows that the greatest adsorbed concentration of malachite green dye solution on LDH Zn-Al adsorbent, magnetic biochar, and LDH Zn-Al/magnetic biochar composite occurs at pH 8. The optimum pH of malachite green dye is at neutral pH, this is due to the effect of equilibrium on the solution. At the optimum pH, too acidic or too basic conditions will experience protonation and the complexes formed will dissociate. It can be seen that the pH pzc and pH optimum have a difference, this can mean that the adsorption that occurs is chemical. Zain et al. (2023) reported that at pH 8 a biocomposite made of chitosan, sepiolite clay, and algae absorbed malachite green with a maximum adsorption capacity of 515.7 mg/g. Malachite green dye adsorption on the surface of chitosan/sepiolite clay/algae biocomposite is thought to be caused by a variety of interactions, including electrostatic, H-bonding, and n- interactions. As a result, by altering the solution's pH, this pH-sensitive chitosan/sepiolite clay/algae biocomposite exhibits a strong affinity for capturing both cationic and anionic dyes (Zain et al., 2023).

3.3 Characterization

The successful development of Zn-Al LDH adsorbent material, magnetic biochar, and Zn-Al LDH composite/ magnetic biochar is shown from the characterization results of XRD, FT-IR, BET, and VSM analysis. Synthesis of Zn-Al LDH material, magnetic biochar, and Zn-Al LDH composite/ magnetic biochar has diffractogram peaks of layered double hydroxide matched with JCPDS No. 48.2023 data for Zn-Al (Siregar et al., 2022). The characterization results of Zn-Al LDH, magnetic biochar, and composite LDH Zn-Al/magnetic biochar are presented in Figure 3.

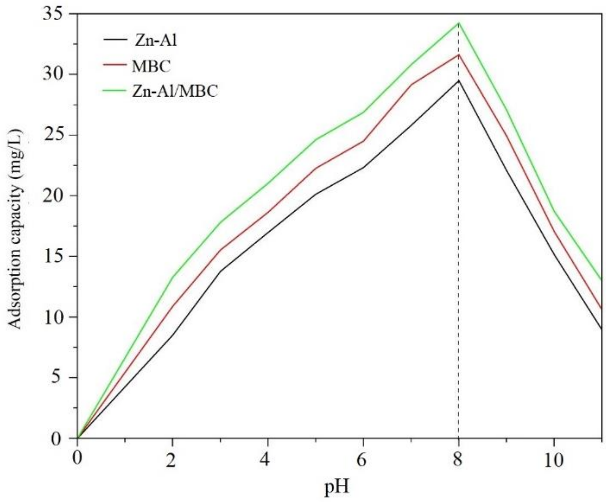

Figure 2. pH on adsorption of malachite green

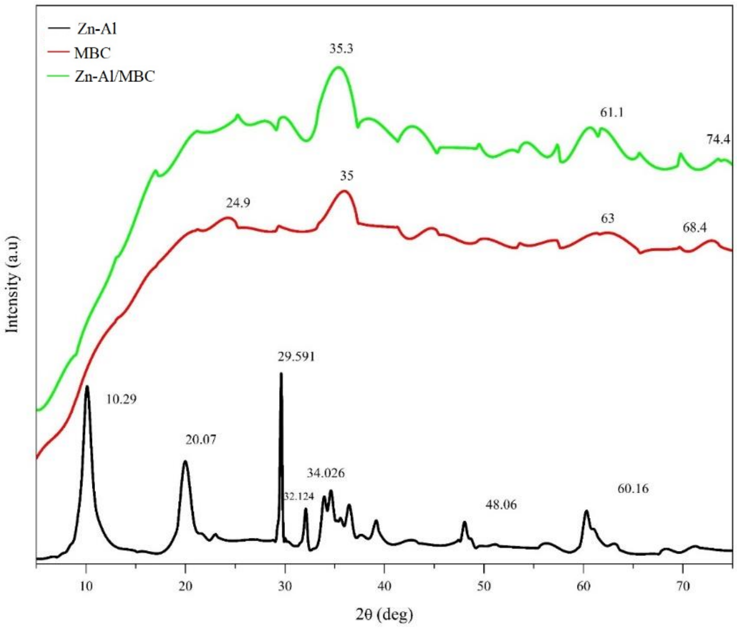

Figure 3. X-ray diffractogram of adsorbents

Typical diffractogram patterns of Zn-Al layered double hydroxide material with angles at 2θ, namely, diffraction peaks at 10.29°, 20.07°, 29.59°, 32.12°, 34.02°, 48.06°, and 60.16° allocated to planes (003), (006), (101), (012), (015), (107), and (110), were detected from XRD patterns. Based on the diffraction peaks the formation of the Zn-Al material structure follows the JCPDS file No 48-1023. According to Palapa et al. (2019), the double diffraction peak found at an angle of 60° is a typical diffraction pattern indicating that the Zn-Al layered double hydroxide material contains anions in the interlayer. Figure 3 explains that the biochar magnet has an angle at 2θ, namely the diffraction peaks at 24.9°, 35°, 63°, and 68.4° for the planes (220), (311), (422), and (440), respectively, while in the layered double hydroxide Zn-Al/magnetic biochar composite, the diffraction angle peaks are shown at 35.3° and 61.1° for the planes (311), and (110), respectively. This explains that magnetic biochar and layered double hydroxide Zn-Al/magnetic biochar composite have been successfully synthesized based on JCPDS file No.19-0619 (Ahmad et al., 2023; Fitri and Ardiansyah, 2023).

The successful synthesis of Zn-Al LDH material, magnetic biochar, and Zn-Al/magnetic biochar layered double hydroxide composite is also supported through FT-IR spectra presented in Figure

4. In Figure 4, there are vibrational peaks at wave numbers 3,441 cm^{-1}, 3,425 cm^{-1}, and 3,448 cm^{-1} this indicates the presence of O-H groups from water molecules in Zn-Al, magnetic biochar, and composite LDH Zn-Al/magnetic biochar. Wave numbers 2,376 cm^{-1} and 2,422 cm^{-1} on composite LDH Zn-Al/magnetic biochar, magnetic biochar, and Zn-Al indicate the presence of C≡C. In the composite LDH Zn-Al/magnetic biochar and magnetic biochar, there are wave numbers of 1,620 cm^{-1} and 1,635 cm^{-1} on the LDH indicating the presence of carbonyl groups C=O (Siregar et al., 2021).

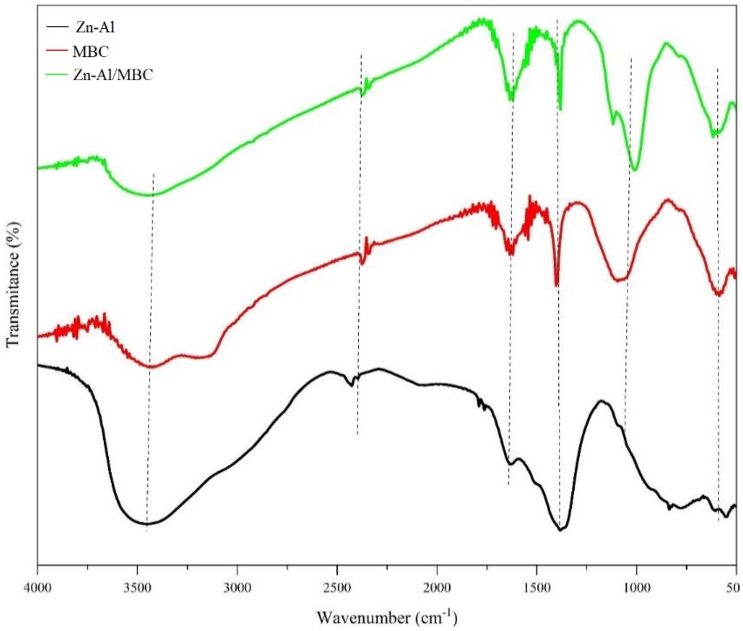

Figure 4. FTIR of adsorbents

In the Zn-Al layered double hydroxide, there is a wave number of 1,381 cm^{-1} indicating the vibration of the NO_3^- group, and wave numbers from 609 to 840 cm^{-1} indicating the presence of M-O vibrations in the form of Zn-O and Al-O. The wave number at 1,404 cm^{-1} in magnetic biochar indicates the presence of C-H carbon groups, at wave number 1,095 cm^{-1} there are C-O vibrations, and at wave number 586 cm^{-1} indicates the presence of magnetic Fe-O. The layered double hydroxide Zn-Al/magnetic biochar composite has wave numbers 1,110-1,120 cm^{-1} indicating the presence of aliphatic amines and wave numbers 580 cm^{-1} indicating the presence of M-O vibrations in Zn-O and Al-O. So it can be said that the synthesis of LDH Zn-Al, biochar magnet, and composite LDH Zn-Al/magnetic biochar has been successfully carried out (Ahmad et al., 2023; Rahmadan et al., 2021).

Using nitrogen adsorption and desorption, BET analysis is performed to learn more about a material's surface area and pore dispersion (Bagheri et al., 2021). Table 1 lists the outcomes of nitrogen adsorption and desorption tests on each adsorbent. The table shows that after modification into a layered double hydroxide Zn-Al/magnetic biochar composite, the surface area increased. This increase occurs because the layered double hydroxide materials have properties that allow them to expand more when composited in an aqueous medium.

The nitrogen adsorption-desorption isotherms for the different adsorbents utilized are shown on the graph in Figure 5. A hysteresis phenomena is depicted in the illustration. All the materials, i.e., LDH Zn-Al, magnetic biochar, and composite LDH Zn-Al/magnetic biochar, follow type IV in the nitrogen adsorption-desorption isotherm curve. Type IV indicates that the material belongs to the mesoporous category because the desorption curve is different from the adsorption curve, resulting in a hysteresis phenomenon. According to IUPAC, mesoporous materials have pore sizes between 2 to 50 nm. The isotherm graphs of various materials, Zn-Al LDH, biochar magnetic, and composite LDH Zn-Al/magnetic biochar are grouped into H2 type. According to Hu et al. (2020) type H2 indicates that the material has a mesoporous structure with pores that have wide loops.

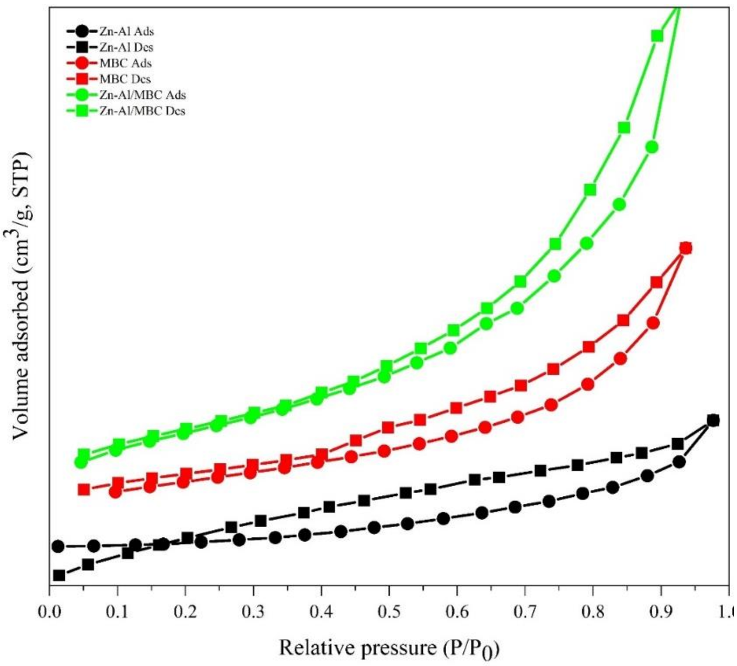

Figure 5. Graph nitrogen adsorption-desorption isotherms of adsorbents

Table 1 displays data on the surface area, pore volume, and pore diameter of the adsorbent materials. The Zn-Al LDH has a surface area of 9.621 m^2/g, while the surface area of magnetic biochar is 81.843 m^2/g. However, after undergoing the modification process into a layered double hydroxide Zn-Al/magnetic biochar composite material, the surface area of the adsorbent successfully increased to 99.473 m^2/g. It can be seen that the higher the carbon content in the material, the larger the surface area. The information in Table 1 also demonstrates that the relationship between surface area and pore volume is direct. In other words, the pore volume increases with surface area. However, there is a trend in the pore diameter size that is inversely related to the surface area and pore volume. The pore diameter gets narrower as the surface area grows in proportion to the pore volume. The Zn-Al material has the smallest surface area, which is 9.621 m^2/g, but has a pore volume of 0.017 cm^3/g. Although it has a small surface area, the pore diameter size in this material is the largest, reaching 12.094 nm. The XRD, FTIR, and BET characterization results proved that the Zn-Al LDH material, magnetic biochar, and Zn-Al/magnetic biochar layered double hydroxide composite have a stable structure. The modification process of this composite material successfully increased the surface area of the Zn-Al starting material.

Table 1. Adsorption-desorption isotherm analysis results of Zn-Al layered double hydroxide material, magnetic biochar, and Zn-Al layered double hydroxide material/magnetic biochar composite

Materials	Surface area (m^2/g)	Volume pore (cm^3/g)	Diameter pore (nm)
Zn-Al	9.621	0.017	12.094
Magnetic	81.843	0.127	4.136
Komposit	99.473	0.238	4.802

VSM (Vibrating Sample Magnetometer) characterization was performed to help understand the magnetic properties of biochar magnetic material and Zn-Al/magnetic biochar layered double hydroxide composite. The Hysteresis loop obtained can be seen in Figure 6. where the Hysteresis loop of magnetization appears like an S. Based on Figure 6 explaining the soft magnetic properties of the magnetite formed, it is observed that in the magnetic biochar and the layered double hydroxide Zn-Al/magnetic biochar composite, the magnetization is completely saturated at a value of 13.04 emu/g for pure magnetite and 9.67 emu/g in the composite. Coercivity (Hci), Magnetization (Ms), and Retentivity (Mr) values for magnetic biochar and layered double hydroxide Zn-Al/magnetic biochar composites, obtained from VSM.

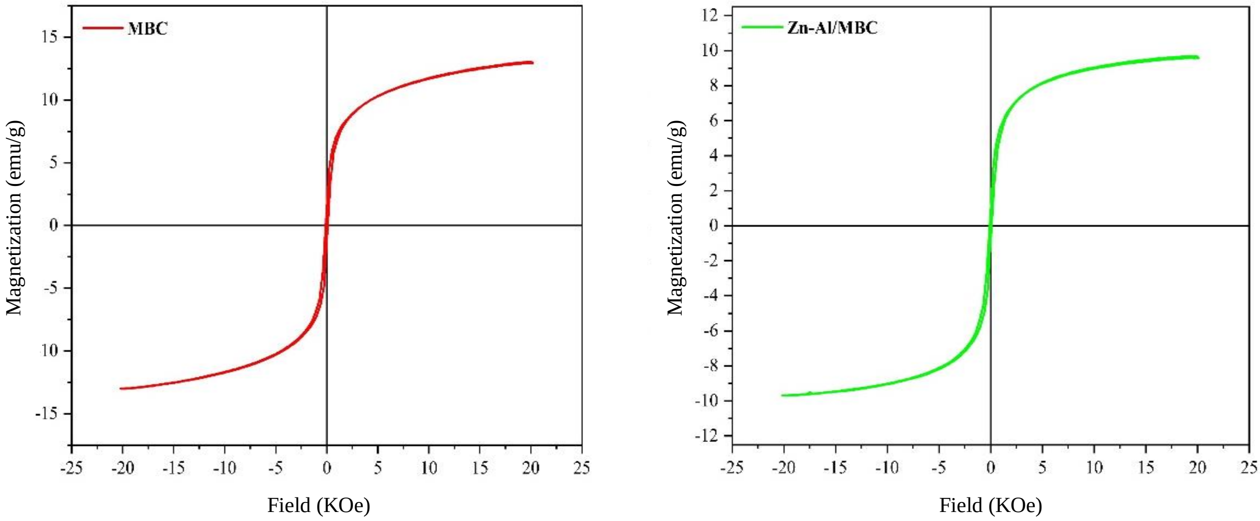

Figure 6. Graph vibrating sample magnetometer of adsorbents

The sharp decrease in Ms value for the layered double hydroxide Zn-Al/magnetic biochar composite may be due to the magnetic incorporation of biochar in the LDH Zn-Al framework, the LDH Zn-Al wall acts as a shield for the magnetic strength of Fe_3O_4. The low saturation magnetization in the composite may be due to the dispersion of nanoparticles in the layered double hydroxide Zn-Al matrix. The particle weight used for magnetic measurements is constant, hence the decrease in saturation magnetization is due to the increase in the amount of layered double hydroxide present in the magnetic composite layer. The layered double hydroxide on the surface of the magnetic composite decreases the surface moment resulting in a reduction in the magnetic moment in the magnetic composite. The magnetic composite has good magnetic stability so it has the ability an adsorption liquid waste. The magnetic composite also has the advantage of making regeneration easier when separating the adsorbent from the adsorbate. Figure 7 is a sample of magnetic biochar and layered double hydroxide Zn-Al/magnetic biochar composite.

Figure 7. Sample adsorbents of (a) magnetic biochar and (b) layered double hydroxide Zn-Al/magnetic biochar composite

3.4 Effect of time and kinetics

The adsorption ability of the prepared materials was proven through several parameters such as adsorption kinetics and thermodynamics. Kinetic parameters were carried out by making variations in adsorption time from 0 to 180 min which can be seen in Figure 8. The closest distance between the Qe_{exp} and Qe_{calc} values in Table 2 and the highest linear regression value are used to determine the PFO and PSO kinetic models (Sheikhmohammadi et al., 2019). While the PSO kinetic model assumes that the active sites of the adsorbent are available more than the potential bonding between the adsorbent and the adsorbate that occurs, the PFO kinetic model assumes that the bonding between the adsorbent and the adsorbate that occurs is proportional to the available active sites (Aqdam et al., 2021). The results of the variation of contact time of malachite green dye on layered double hydroxide Zn-Al and magnetic biochar seen in Figure 8 show that the equilibrium time is reached at 70 min and on the layered double hydroxide Zn-Al/magnetic biochar composite at 40 min. The equilibrium time explains that the adsorption process has reached the optimum time where, after this time is reached, the resulting adsorption ability is not much different, resulting in a flat curve. This also shows the tendency towards the kinetics model of the adsorption process. It can be seen that all materials and their modifications are more likely to follow the PSO kinetics model than PFO. This determination is also evidenced by the data of linear regression values in Table 2.

Linear regression data on malachite green dye against Zn-Al ldh adsorbent, magnetic biochar, and composite LDH Zn-Al/magnetic biochar showed almost the same values of 0.9766, 0.9865, and 0.9896 in the PSO kinetic model. Based on this, it can be seen that the LDH Zn-Al, magnetic biochar, and LDH Zn-Al/magnetic biochar composites tend to follow the PSO kinetics model. The malachite green dye adsorbed using layered double hydroxide Zn-Al adsorbent, magnetic biochar, and layered double hydroxide Zn-Al/magnetic biochar composite all tend to follow the PSO kinetics model which can be seen from the linear regression values that are closer to 1. Based on these findings, it is established that the adsorption process happens on the active sites of the adsorbent that are available rather than the potential for adsorbent and adsorbate bonding. The Qe_{exp} value of each adsorbent, which is closer to Qe_{calc} from the PSO kinetics model, serves as more support for this.

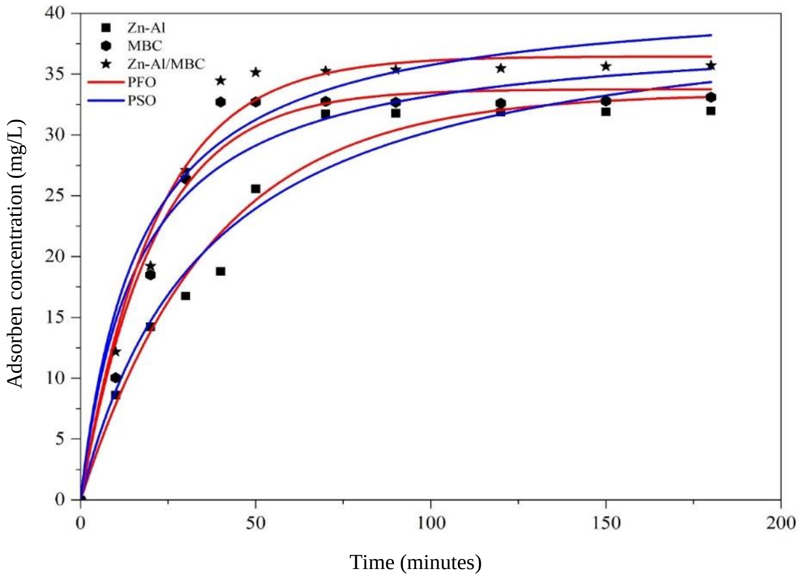

Figure 8. Model for adsorption kinetics

Table 2. Kinetic model of adsorption of malachite green dye on layered double hydroxide Zn-Al, magnetic biochar, and layered double hydroxide Zn-Al/magnetic biochar composite

Dye	Materials	Qe_{exp}	PFO			PSO		
		mg/g	k_1	Qe_{calc}	R^2	k_2	Qe_{calc}	R^2
Malachite green	Zn-Al	31.971	0.0325	20.8161	0.647	0.0008	39.5257	0.9766
	Magnetic biochar	33.114	0.0207	7.0340	0.4324	0.0021	36.2319	0.9865
	Composite	35.721	0.0272	10.7795	0.5991	0.0097	30.0030	0.9896

3.5 Effect of isotherms and thermodynamic studies

The adsorption isotherm and thermodynamic parameters were calculated using the effects of concentration and temperature on the adsorption of the dye malachite green. The Langmuir and Freundlich isotherm models are the two most often employed isotherm models. The Langmuir isotherm model, which presupposes the active side and energy contained on the adsorbent surface are homogeneous, explains that the adsorption process occurs chemically (chemisorption). In contrast to the Freundlich isotherm, which assumes that the adsorption process occurs physically (physisorption), this results in the interaction between the adsorbent and adsorbate only occurring in a single layer (monolayer) of the materials, resulting in a strong bond between the active side of the adsorbent and the adsorbate, namely the dye.

This assumes that the adsorption process occurs in many layers (multilayer). Table 3 shows the isotherm model can be done by looking at the linear regression value (R^2) which is closer to 1. The composite LDH Zn-Al/magnetic biochar and magnetic biochar tend to follow the Freundlich isotherm model, while the Zn-Al layered double hydroxide adsorbent and magnetic biochar tend to follow the Langmuir isotherm model, according to the data in Table 3. This is a result of the R^2 values becoming closer to 1. Table 3 also provides information on the adsorption capacity (Qm).

Table 3 shows the capacity of adsorption (Qm) of dye malachite green on Zn-Al layered double hydroxide, biochar magnetic, and composite LDH Zn-Al/magnetic biochar. The largest adsorption capacity of 25.907 mg/g occurs in LDH Zn-Al/magnetic biochar composite at 60°C, followed by magnetic biochar at 60°C with an adsorption capacity (Qm) of 15.552 mg/g, and layered double hydroxide Zn-Al at 60°C with an adsorption capacity (Qm) of 14.472 mg/g. The capacity of NiAl LDH/BC of 15.1 mg/g in the study of Palapa et al. (2022) achieved a satisfactory performance. This illustrates how effectively NiAl LDH/BC removes MG dye from aqueous samples. In Table 3, the Langmuir constant (KL) value is calculated to determine the strength of interaction between adsorbate and adsorbent surface. Data from Table 3 shows the KL value for each adsorbent tends to increase with increasing temperature. This indicates that the interaction between adsorbate and adsorbent is strong. This confirms that the layered double hydroxide Zn-Al/magnetic biochar composite has a greater adsorption capacity than its constituent materials, namely layered double hydroxide Zn-Al and magnetic biochar.

Table 3. Adsorption isotherm parameters of malachite green color on layered double hydroxide Zn-Al, magnetic biochar, and layered double hydroxide Zn-Al/magnetic biochar composites

Adsorbents	T(°C)	Qm	Model isotherms adsorption				
			Langmuir		Freundlich		
			Kl	R^2	n	Kf	R^2
ZnAl	30	0.227	0.015	0.9909	0.081	1.2331	0.8485
	40	0.361	0.017	0.9206	0.076	1.1015	06966
	50	0.432	0.018	0.5217	0.091	5.2601	0.2507
	60	14.472	0.030	0.9958	0.415	8.6139	0.9685
Magnetic	30	0.278	0.018	0.8785	0.047	2.4717	0.9942
	40	0.467	0.021	0.3777	0.049	3.9445	0.2615
	50	3.034	0.030	0.4541	0.162	1.7782	0.654
	60	15.552	0.085	0.9975	1.448	3.426	0.7634
Composites	30	2.125	0.019	0.9128	0.118	8.5703	0.9835
	40	2.124	0.020	0.8173	0.102	7.1285	0.9317
	50	4.274	0.034	0.5655	0.217	4.2785	0.7138
	60	25.907	0.143	0.9902	2.515	1.4564	0.5089

Enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) are three thermodynamic parameters that were identified during the adsorption of green malachite dye and are shown in Table 4-6. To ascertain whether the adsorption process is endothermic or exothermic, the enthalpy value (ΔH) in dye adsorption is measured. The entropy value (ΔS) of dye adsorption is determined to determine the degree of disorder during the process. Whether or not the adsorption process is spontaneous can be determined by looking at the value of Gibbs free energy (ΔG).

Table 4 shows the thermodynamic parameter data of malachite green dye adsorption on ZnAl layered double hydroxide adsorbent. In Table 4, the enthalpy (ΔH) is positive for layered double hydroxide ZnAl, which is 2.037-14.828 KJ/mol. This indicates that, during the adsorption phase, the reaction is endothermic. The entropy value (ΔS) is positive at 0.007-0.054 KJ/mol. This suggests that there is little chaos during the adsorption process. Given that the Gibbs free energy (ΔG) is negative, the adsorption of the dye malachite green occurs voluntarily. The thermodynamic parameter information for the adsorption of malachite green on biochar magnetic is displayed in Table 5. Biochar magnetic also exhibits a positive enthalpy value (ΔH) of 9.957-25.107 kJ/mol, similar to Zn-Al layered double hydroxide. This indicates that the reaction that takes place during the adsorption process is endothermic. The entropy value (ΔS) on the biochar magnetic also shows a positive value of 0.033-0.90 j/mol/K. This indicates that the biochar magnetic when adsorbing green malachite has a small degree of irregularity during the adsorption process. The Gibbs free energy (ΔG) of the biochar magnetic when adsorbing green malachite is also negative, indicating that the adsorption process takes place spontaneously.

Table 4. Thermodynamic parameter data of adsorption of malachite green dye on layered double hydroxide adsorbent ZnAl

Concentration (mg/L)	Temperature (K)	Qe (mg/g)	ΔH (kJ/mol)	ΔS (J/K mol)	ΔG (kJ/mol)
	303	25.471	2.037	0.007	-0.080
	313	25.900			-0.150
50	323	26.150			-0.220
	333	26.400			-0.290
	303	31.079	8.653	0.029	-0.096
	313	32.186			-0.384
60	323	33.614			-0.673
	333	35.757			-0.962
	303	39.329	11.047	0.038	-0.531
	313	41.579			-0.914
70	323	43.329			-1.296
	333	46.186			-1.678
	303	48.150	12.899	0.046	-0.981
	313	51.079			-1.439
80	323	53.757			-1.897
	333	56.614			-2.355
	303	58.579	14.828	0.054	-1.481
	313	62.150			-2.020
90	323	65.579			-2.558
	333	68.614			-3.096

Table 5. Thermodynamic parameter data of adsorption of malachite green dye on biochar magnetic adsorbent

Concentration (mg/L)	Temperature (K)	Qe (mg/g)	ΔH (kJ/mol)	ΔS (J/K mol)	ΔG (kJ/mol)
	303	25.971	9.957	0.033	-0.167
	313	27.400			-0.501
50	323	29.186			-0.836
	333	30.257			-1.170
	303	34.293	14.149	0.049	-0.697
	313	37.150			-1.187
60	323	39.293			-1.677
	333	41.471			-2.167
	303	44.043	16.786	0.059	-1.217
	313	46.900			-1.811
70	323	50.471			-2.405
	333	52.971			-2.999
	303	53.043	19.714	0.070	-1.628
	313	56.614			-2.333
80	323	61.614			-3.037
	333	63.757			-3.741
	303	62.900	25.107	0.090	-2.026
	313	67.900			-2.922
90	323	74.329			-3.817
	333	76.471			-4.713

Table 6. Thermodynamic parameter data of adsorption of malachite green dye on layered double hydroxide ZnAl/magnetic biochar composite adsorbent

Concentration (mg/L)	Temperature (K)	Qe (mg/g)	ΔH (kJ/mol)	ΔS (J/K mol)	ΔG (kJ/mol)
50	303	28.829	9.505	0.034	-0.652
	313	29.543			-0.987
	323	30.257			-1.323
	333	33.114			-1.658
60	303	37.221	14.810	0.052	-1.074
	313	38.650			-1.599
	323	40.793			-2.123
	333	44.329			-2.647
70	303	46.829	16.500	0.060	-1.577
	313	48.257			-2.173
	323	52.650			-2.770
	333	54.757			-3.367
80	303	55.507	20.605	0.074	-1.876
	313	57.650			-2.618
	323	62.864			-3.360
	333	65.900			-4.102
90	303	64.757	29.316	0.104	-2.070
	313	66.543			-3.106
	323	76.471			-4.142
	333	78.614			-5.178

Table 6 shows the thermodynamic parameter data of green malachite dye adsorption on composite LDH Zn-Al/magnetic biochar adsorbent material. Similar to the LDH Zn-Al and magnetic biochar, the composite LDH Zn-Al/magnetic biochar adsorbent also has a positive enthalpy value (ΔH) of 9.505-29.316 kJ/mol. This informs that when adsorbing green malachite dye, the composite LDH Zn-Al/magnetic biochar has an endothermic reaction during the adsorption process. The entropy value (ΔS) of the composite LDH Zn-Al/magnetic biochar is the same as the LDH Zn-Al and magnetic biochar which shows a positive value of 0.034-0.104 j/mol/K. This indicates that the LDH Zn-Al/magnetic biochar composite, when adsorbing malachite green dye, has a small degree of disorder. The Gibbs free energy (ΔG) of the layered double hydroxide ZnAl/magnetic biochar composite is also the same as the layered double hydroxide Zn-Al and magnetic biochar when the adsorption of malachite green is negative, indicating that the adsorption process takes place spontaneously. Table 7 provides information on the adsorption capacities that have been made by other researchers.

Table 7. Adsorption of malachite green using other adsorbents

Adsorbent	Adsorption capacity (mg/g)	References
Rice husk/MnO	68.534	Emilia et al. (2023)
NiFe-POM	8.81	Lesbani et al. (2020)
Apricot carbon activated	17.60	Abbas (2020)
Magnetic GO/Fe_3O_4	59	Li et al. (2021)
Magnetic reduced graphene oxide nanocomposite	77.1	Sadegh et al. (2021)
M-Sp	69.444	Hasanah et al. (2023)
Camphor leaf	68.9	Hu et al. (2019)
MBC	76.471	This Study
Zn-Al/MBC	78.614	This Study

3.6 Adsorbents' capacity for re-use

By employing ultrasonics to remove the adsorbate from the adsorbent surface, regeneration is the process of using the materials again. The regeneration process can be done through adsorption and desorption steps first. After going through the adsorption and desorption steps, 0.2 g aliquots of LDH Zn-Al, magnetic biochar, and composite LDH Zn-Al/magnetic biochar were used to adsorb malachite green dye. The results of the regeneration of LDH Zn-Al, magnetic biochar, and composite LDH Zn-Al/magnetic biochar against malachite green dye can be seen in Figure 9. Figure 9 shows that the composite LDH Zn-Al/magnetic biochar against malachite green dye can adsorb as much as 92.25% of maximum capacity after the first regeneration, 82.61% after the second regeneration, 72.20% after the third regeneration, 68.47% after the fourth regeneration, and 55.46% after the fifth regeneration. The magnetic biochar was able to adsorb as much as 85.05% malachite green dye after the first regeneration, 79.74% after the second regeneration, 67.89% after the third regeneration, 64.15% after the fourth regeneration, and 51.87% after the fifth regeneration. The Zn-Al layered double hydroxide material had the smallest adsorption ability to malachite green dye compared to the other two adsorbents, namely, 79.24% after the first regeneration, 61.78% after the second regeneration, third regeneration 46.34%, fourth regeneration 37.16% and fifth regeneration 29.60%. This can be seen from the instability in Figure 9 that results from the repeated use of LDH Zn-Al, magnetic biochar, and composite LDH Zn-Al/magnetic biochar. Adsorption of malachite green by Amri and Hanifah (2023) using graphene oxide material from the first cycle to the fifth cycle decreased by 40.19%. This shows that adsorption with composite LDH Zn-Al/magnetic biochar is more effective in regeneration.

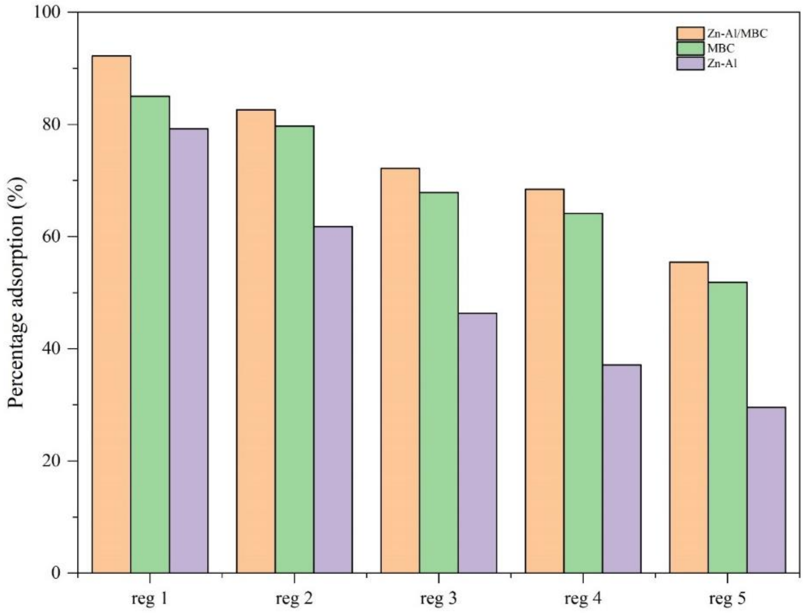

Figure 9. Reusability of adsorbent materials

3.7 Mechanism of malachite green adsorption

Figure 10 shows the adsorption mechanism of malachite green with the composite layered double hydroxide Zn-Al/magnetic biochar. Physical adsorption explains how malachite green can enter the pores of biochar and bind through van der Waals forces and capillary forces. Biochar with a large pore structure will provide a large surface area for malachite green to adsorb. Chemical adsorption allows composite layered double hydroxide on biochar to chemically interact with malachite green. This may involve the formation of chemical bonds or electrostatic interactions between the functional groups on malachite green and the layered double hydroxide groups on the hydroxy layer. These interactions can increase adsorption power and adsorption stability. Ion exchange occurs where malachite green is a charged compound, the layered double hydroxide on biochar can act as an ion exchange site, where positively charged malachite green can exchange with negative ions on the LDH, increasing the adsorption of the compound. The adsorption capacity is optimized by applying optimum pH, optimum time, optimum concentration, and temperature (Palapa et al., 2022; Ahmad et al., 2017; Rahmadan et al., 2021; Dai et al., 2022).

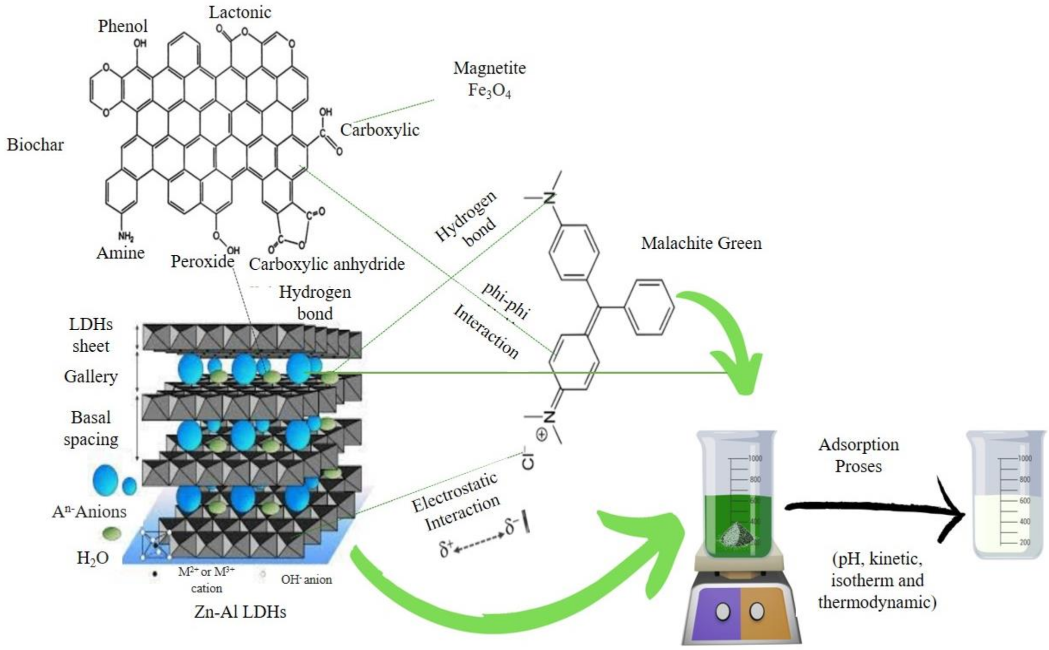

Figure 10. Adsorption mechanism of composite layered double hydroxide Zn-Al/magnetic biochar

4. CONCLUSION

According to this study's XRD, FTIR, BET, and VSM analyses, the Zn-Al, magnetic biochar, and Zn-Al/magnetic biochar composite were effectively synthesized. Regarding pH, Zn-Al and magnetic biochar had a pH of 6, whereas the composite of these two materials was pH 7. For Zn-Al, magnetic biochar, and composite Zn-Al/magnetic biochar, pH 8 is the ideal value for adsorption of malachite green. The PSO (pseudo-second order) kinetics model serves as the basis for this adsorption. The reaction is typically endothermic, the Gibbs Free Energy (ΔG) tends to occur spontaneously, and the isotherm parameters on Zn-Al, magnetic biochar, and Zn-Al/magnetic biochar composite against malachite green dye tend to follow the Langmuir isotherm model. The adsorption capacity of the magnetic Zn-Al/biochar composite at 60℃ was found to be up to 25.907 mg/g. Regenerated magnetic Zn-Al/biochar composite showed superior performance of up to 92.25% of initial capacity.

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REFERENCES

Abbas M. Experimental investigation of activated carbon prepared from apricot stones material (ASM) adsorbent for removal of malachite green (MG) from aqueous solution. Adsorption Science and Technology 2020;38(1-2):24-45.

Ahmad MA, Afandi NS, Bello OS. Optimization of process variables by response surface methodology for malachite green dye removal using lime peel activated carbon. Applied Water Science 2017;7(2):717-27.

Ahmad N, Arsyad FS, Royani I, Lesbani A. Charcoal activated as template Mg/Al layered double hydroxide for selective adsorption of direct yellow on anionic dyes. Results in Chemistry 2023;5:Article No. 100766.

Amri A, Hanifah Y. Synthesis of graphene oxide using hummers method as adsorbent of malachite green dye. Indonesian Journal of Material Research 2023;1(1):29-34.

Aqdam SR, Otzen DE, Mahmoodi NM, Morshedi D. Adsorption of azo dyes by a novel bio-nanocomposite based on whey protein nanofibrils and nano-clay: Equilibrium isotherm and kinetic modeling. Journal of Colloid and Interface Science 2021;602:490-503.

Badhai P, Kashyap S, Behera SK. Adsorption of phenol red onto GO-Fe_3O_4 hybrids in aqueous media. Environmental Nanotechnology, Monitoring and Management 2020;13: Article No. 100282.

Bagheri A, Hoseinzadeh H, Hayati B, Mahmoodi NM, Mehraeen E. Post-synthetic functionalization of the metal-organic framework: Clean synthesis, pollutant removal, and antibacterial activity. Journal of Environmental Chemical Engineering 2021;9(1):Article No. 104590.

Bouteraa S, Saiah FBD, Hamouda S, Bettahar N. Zn-M-CO_3 layered double hydroxides (M=Fe, Cr, or Al): Synthesis, characterization, and removal of aqueous Indigo Carmine.

Bulletin of Chemical Reaction Engineering and Catalysis 2020;15(1):43-54.

Cheng S, Zhao S, Xing B, Liu Y, Zhang C, Xia H. Preparation of magnetic adsorbent-photocatalyst composites for dye removal by the synergistic effect of adsorption and photocatalysis. Journal of Cleaner Production 2022;348:Article No. 131301.

Dai X, Yi W, Yin C, Li K, Feng L, Zhou Q, et al. 2D-3D magnetic NiFe layered double hydroxide decorated diatomite as multi-function material for anionic, cationic dyes, arsenate, and arsenite adsorption. Applied Clay Science 2022;229:Article No. 106664.

dos Santos TC, Mancera RC, Rocha MV, da Silva AF, Furtado IO, Barreto J, et al. CO_2 and H_2 adsorption on 3D nitrogen-doped porous graphene: Experimental and theoretical studies. Journal of CO_2 Utilization 2021;48:Article No. 101517.

Emilia D, Hakim YM, Mohadi R. Mangan oxide-assisted in biochar improvement and application in malachite green removal. Indonesian Journal of Material Research 2023; 1(2):35-43.

Faggio N, Zuppardi F, Staiano C, Poggetto GD, D'Ayala GG, Cerruti P. Removal of anionic and cationic dyes from aqueous solution using thermo- and pH-responsive amphiphilic copolymers. Journal of Water Process Engineering 2022; 49:Article No. 103107.

Fitri ES, Ardiansyah R. Study and characterization of hydrochar from duku (*Lansium domesticum*) peel. Indonesian Journal of Material Research 2023;1(2):44-50.

Hasanah M, Juleanti N, Priambodo A, Arsyad F, Lesbani A, Mohadi R. Utilization of rambutan peel as a potential adsorbent for the adsorption of malachite green, procion red, and congo red dyes. Ecological Engineering and Environmental Technology 2022;23(3):148-57.

Hasanah M, Wijaya A, Arsyad FS, Mohadi R, Lesbani A. Preparation of c-based magnetic materials from fruit peel and hydrochar using snake fruit (*Salacca zalacca*) peel as adsorbents for the removal of malachite green dye. Environment and Natural Resources Journal 2023;21(1):67-77.

Ho ZH, Adnan LA. Phenol removal from aqueous solution by adsorption technique using coconut shell activated carbon. Tropical Aquatic and Soil Pollution 2021;1(2):98-107.

Hosseinabadi-Farahani Z, Hosseini-Monfared H, Mahmoodi NM. Graphene oxide nanosheet: Preparation and dye removal from binary system colored wastewater. Desalination and Water Treatment 2015;56(9):2382-94.

Hu H, Wageh S, Al-Ghamdi AA, Yang S, Tian Z, Cheng B, et al. NiFe-LDH nanosheet/carbon fiber nanocomposite with enhanced anionic dye adsorption performance. Applied Surface Science 2020;5(11):Article No. 145570.

Hu Y, Zhu Y, Zhang Y, Lin T, Zeng G, Zhang S, et al. An efficient adsorbent: Simultaneous activated and magnetic ZnO doped biochar derived from camphor leaves for ciprofloxacin adsorption. Bioresource Technology 2019;288:Article No. 121511.

Lee SY, Choi JW, Song KG, Choi K, Lee YJ, Jung KW. Adsorption and mechanistic study for phosphate removal by rice husk-derived biochar functionalized with Mg/Al-calcined layered double hydroxides via co-pyrolysis. Composites Part B: Engineering 2019;176:Article No. 107209.

Lesbani A, Taher T, Palapa

NR, Mohadi R, Rachmat A, Mardiyanto. Preparation and utilization of Keggin-type polyoxometalate intercalated Ni-Fe layered double hydroxides for enhanced adsorptive removal of cationic dye. SN Applied Sciences 2020;2(3):Article No. 470.

Li W, Xu M, Cao Q, Luo J, Yang S, Zhao G. Magnetic GO/Fe_3O_4 for rapid malachite green (MG) removal from aqueous solutions: A reversible adsorption. RSC Advances 2021; 11(32):19387-94.

Li L, Cheng M, Qin L, Almatrafi E, Yang X, Yang L, et al. Enhancing hydrogen peroxide activation of CuCo layered double hydroxide by compositing with biochar: Performance and mechanism. Science of the Total Environment 2022;828:Article No. 154188.

Liao W, Zhou X, Cai N, Chen Z, Yang H, Zhang S, et al. Simultaneous removal of cadmium, lead, chromate by biochar modified with layered double hydroxide with sulfide intercalation. Bioresource Technology 2022;360:Article No. 127630.

Lv HW, Jiang HL, He FA, Hu QD, Zhong ZR, Yang YY. Adsorption of anionic and cationic dyes by a novel crosslinked cellulose-tetrafluoroterephthalonitrile-tannin polymer. European Polymer Journal 2022;180:Article No. 111602.

Mahmoodi NM, Mokhtari-Shourijeh Z. Preparation of aminated nanoporous nanofiber by solvent casting/porogen leaching technique and dye adsorption modeling. Journal of the Taiwan Institute of Chemical Engineers 2016;65:378-89.

Mahmoodi NM, Hosseinabadi-Farahani Z, Chamani H. Dye adsorption from single and binary systems using NiO-MnO_2 nanocomposite and artificial neural network modeling. Environmental Progress and Sustainable Energy 2017;36(1):111-9.

Mahmoodi NM, Karimi B, Mazarji M, Moghtaderi H. Cadmium selenide quantum dot-zinc oxide composite: Synthesis, characterization, dye removal ability with UV irradiation, and antibacterial activity as a safe and high-performance photocatalyst. Journal of Photochemistry and Photobiology B: Biology 2018;188:19-27.

Mohadi R, Palapa NR, Lesbani A. Preparation of ca/al-layered double hydroxides/biochar composite with high adsorption capacity and selectivity toward cationic dyes in aqueous. Bulletin of Chemical Reaction Engineering and Catalysis 2021;16(2):244-52.

Mokhtari-Shourijeh Z, Langari S, Montazerghaem L, Mahmoodi NM. Synthesis of porous aminated pan/pvdf composite nanofibers by electrospinning: characterization and direct red 23 removals. Journal of Environmental Chemical Engineering 2020;8(4):Article No. 103876.

Normah N, Palapa NR, Taher T, Mohadi R, Utami HP, Lesbani A. The ability of composite Ni/Al-carbon-based material toward readsorption of iron(II) in aqueous solution. Science and Technology Indonesia 2021;6(3):156-65.

Palapa NR, Rahayu BR, Taher T, Lesbani A, Mohadi R. Kinetic adsorption of direct yellow onto Zn/Al and Zn/Fe layered double hydroxides. Science and Technology Indonesia 2019;4(4):Article No. 101.

Palapa NR, Taher T, Rahayu BR, Mohadi R. CuAl LDH / rice husk biochar composite for enhanced adsorptive removal of cationic dye from aqueous solution. Science and Technology Indonesia 2020;16(3):540-8.

Palapa NR, Taher T, Normah N, Lesbani A. NiAl layered double hydroxide/rice husk composite for the efficient removal of malachite green. Indonesian Journal of Chemistry 2022; 22(1):142-56.

Rabeie B, Mahmoodi NM. Heterogeneous MIL-88A on MIL-88B hybrid: A promising eco-friendly hybrid from green synthesis to dual application (Adsorption and photocatalysis) in tetracycline and dye removal. Journal of Colloid and Interface Science 2024;654:495-522.

Rahmadan J, Parhusip V, Palapa NR, Taher T, Mohadi R, Lesbani A. ZnAl-humic acid composite as adsorbent of cadmium(II) from aqueous solution. Science and Technology Indonesia 2021;6(4):247-55

Rathee G, Awasthi A, Sood D, Tomar R, Tomar V, Chandra R. A new biocompatible ternary layered double hydroxide adsorbent for ultrafast removal of anionic organic dyes. Scientific Reports 2019;9(1):Article No. 16225.

Sadegh N, Haddadi H, Arabkhani P, Asfaram A, Sadegh F. Simultaneous elimination of rhodamine B and malachite green dyes from the aqueous sample with magnetic reduced graphene oxide nanocomposite: Optimization using experimental design. Journal of Molecular Liquids 2021; 343:Article No. 117710.

Selvanathan M, Yann KT, Chung CH, Selvarajoo A, Arumugasamy SK, Sethu V. Adsorption of copper(II) ion from aqueous solution using biochar derived from rambutan (*Nephelium lappaceum*) peel: Feedforward neural network modeling study. Water, Air, and Soil Pollution 2017; 228(8):Article No. 299.

Sheikhmohammadi A, Yazdanbakhsh A, Moussavi G, Eslami A, Rafiee M, Sardar M, et al. Degradation and COD removal of trichlorophenol from wastewater using sulfite anion radicals in a photochemical process combined with a biological reactor: Mechanisms, degradation pathway, optimization, and energy consumption. Process Safety and Environmental Protection 2019;123:263-71.

Siregar PMSBN, Palapa NR, Wijaya A, Fitri ES, Lesbani A. Structural stability of Ni/Al layered double hydroxide supported on graphite and biochar toward adsorption of congo red. Science and Technology Indonesia 2021;6(2):85-95.

Siregar PMSBN, Lesbani A, Mohadi R. Mg/Al-chitosan as a selective adsorbent in the removal of methylene blue from aqueous solutions. Science and Technology Indonesia 2022;7(2):170-8.

Vithanage M, Ashiq A, Ramanayaka S, Bhatnagar A. Implications of layered double hydroxides assembled biochar composite in adsorptive removal of contaminants: Current status and future perspectives. Science of the Total Environment 2020;737: Article No. 139718.

Wijaya A, Siregar PMSBN, Priambodo A, Palapa NR, Taher T, Lesbani A. Innovative modified of Cu-Al/c (c=biochar, graphite) composites for removal of procion red from aqueous solution. Science and Technology Indonesia 2021;6(4): 228-34.

Yan J, Li K, Yan J, Fang Y, Liu B. A magnetically recyclable magnetic graphite oxide composite functionalized with polydopamine and β-cyclodextrin for cationic dyes wastewater remediation: Investigation on adsorption performance, reusability, and adsorption mechanism. Applied Surface Science 2022;602:Article No. 154338.

Yuliasari N, Badri AF, Wijaya A, Siregar PMSBN, Amri A, Mardiyanto M, et al. Modification of Mg/Al-LDH intercalated metal oxide (Mg/Al-Ni) to improve the performance of methyl orange and methyl red dyes adsorption process. Science and Technology Indonesia 2022;7(3):275-83.

Zain ZM, Abdulhameed AS, Jawad AH. A pH-sensitive surface of chitosan/sepiolite clay/algae biocomposite for the removal of malachite green and remazol brilliant blue r dyes: Optimization and adsorption mechanism study. Journal of Polymers and the Environment 2023;31:501-18.

Zubair M, Aziz HA, Ihsanullah I, Ahmad MA, Al-Harthi MA. Engineered biochar supported layered double hydroxide-cellulose nanocrystals composite-: Synthesis, characterization, and azo dye removal performance. Chemosphere 2022; 307:Article No. 136054.