Kinetics, Isotherm, and Thermodynamic Study for Ultrafast Adsorption of Azo Dye by an Efficient Sorbent: Ternary Mg/(Al + Fe) Layered Double Hydroxides

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ABSTRACT: The extremely high adsorption efficiency of malachite green (MG) was examined through a series of batch experiments by using Fe3+-doped Mg/Al layered double hydroxides (LDHs). The incorporation of iron into Mg/Al LDH with varying Al + Fe molar ratio of 4 + 1, 3 + 2, 2 + 3, and 1 + 4 increased the adsorption capacity with respect to time. The spectral analysis and N2 sorption studies showed that there was retention of surface morphology in all of the iron-modified LDH samples. The experimental evidences showed that the adsorbent Mg/(Al + Fe) with a molar ratio of 10:2 + 3 had a significant removal, i.e., 99.94% for MG with the initial concentration of 1000 mg L−1 at pH ~ 9 and at room temperature in 5 min. With further increase in iron loading (at ratio 10:1 + 4), there was a decrease in the removal of MG due to the agglomeration of Fe2O3 on the surface. The adsorption process was best fitted to the Freundlich isotherm followed by the pseudo-second-order model. The standard thermodynamic parameters (ΔH°, ΔS°, and ΔG°) were obtained over the temperature range of 20−50 °C. It was observed that the adsorption of MG onto Mg/(Al + Fe) LDH was spontaneous, exothermic, and enthalpy driven in the physisorption mode. A worthy desorption efficiency was achieved by using ethanol and water, which was more than 90% in the three cycles. Maintaining almost the same removal efficiency of MG even after three cycles indicated Mg/(Al + Fe) LDH as a promising material for wastewater treatment. This work was anticipated to open up new possibilities in dealing with anionic dye pollutants.

1. INTRODUCTION

The scarcity of safe drinking water throughout the world has become a grave concern and requires innovative and smart materials to remove toxins from wastewater. The ubiquitousness of dyes in the effluents of textile, paper, plastics, paints, and cosmetics companies are toxic, carcinogenic, and mutagenic to cause serious health hazards and possess threat to aquatic living organisms.1 Malachite green (MG) has become a provocative dye, as it is extensively used in aquaculture, fabrication of leather, silk, and paper, and simultaneously branded as a class II toxic substance.2,3 The removal of harmful dyes has been carried out by various conventional methods, like membrane filtration, photocatalytic degradation, microbiological process, coagulation, flocculation, and adsorption. Among these treatment technologies, adsorption has attracted significant attention for the removal of pollutants from aqueous solutions, owing to its advantages of being technically simple, inexpensive, and noncumbersome, and having sludge-free operational properties and excellent regeneration potential.4 Lately, activated carbon, graphene oxide, and porous carbon materials have exhibited high efficacy as a sorbent for dye removal, but the toxic effect of these nanosorbents are of greater concern.5−7 Hitherto, it remains a challenge for researchers to develop a simple, nontoxic, and efficient adsorbent for practical applications to remove dyes from water.

Layered double hydroxides (LDHs) belong to the family of two-dimensional anionic clays with the general formula [MII]x[MIII]y(OH)z]+x[A−n−z]·n/2yH2O, where MII represents a divalent metal cation, MIII is a trivalent metal cation, A− is an interlayer anion, and x and y are defined as the molar ratio of MII/(MII + MIII) metal ions.8 LDHs display attractive physical and chemical properties including effective dispersion, large specific surface areas, and high anion exchange capacities that make them ideal adsorbents for many cations and anions.9 The multifaceted use of transition-metal-modified LDH for environmental sustainability and energy production has been reported by our team.10 Dodecylsulfate-modified Mg/Al LDH was used to remove polycyclic aromatic hydrocarbons that showed efficient adsorption of hydrocarbons which is fitted well to Freundlich and C-type isotherms.11 The solar light-induced photodegradation of organic pollutants, hydrogen evolution by water splitting, phosphate adsorption, and organic transformation reactions by transition-metal-incorporated LDH systems have been reported by our group.12−18 The effective removal of arsenate and vanadate has been achieved by using...
hydroxylamine formed via the co-precipitation method that removed more than 95% of the toxic anions.\textsuperscript{19}

Various ternary LDHs with combinations of diverse divalent and trivalent metal ions were also reported.\textsuperscript{20,21} The established works on ternary LDHs are limited to definite applications as catalysts in organic transformations and fluorescence sensitivity.\textsuperscript{22,23}

In this paper, we have reported the designing of a ternary Mg/(Al + Fe) LDH and investigated the effect of substituting Fe\textsuperscript{3+} ions into the LDH structure. The main objective of our study is to investigate the effective and fast removal of malachite green (MG) dye by Mg/(Al + Fe) LDH from contaminated water. The adsorption properties of the prepared ternary LDH was explored by studying the effect of various operating parameters, like, pH, dye concentration, temperature, and contact time, on the adsorption process. To know the nature of adsorption, the thermodynamic parameters, like $\Delta H^\circ$, $\Delta S^\circ$, and $\Delta G^\circ$, were also evaluated.

\section*{2. EXPERIMENTAL SECTION}

\subsection*{2.1. Materials.} Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, NaOH, and Na\textsubscript{2}CO\textsubscript{3} were purchased from Merck Chemical. All of the reagents were of analytical grade and used with no further purification. The cationic dye, malachite green (MG), having the chemical formula C\textsubscript{23}H\textsubscript{25}N\textsubscript{2}Cl and molecular weight 364.63 g mol\textsuperscript{-1}, was provided from Loba chemie and used as such. All of the required stock solutions of the chosen concentration were freshly prepared from the stock solution.

\subsection*{2.2. Synthesis of Adsorbent.} The ternary (Mg/Al + Fe) LDH was prepared by the co-precipitation method maintaining a constant ratio of Mg/(Al + Fe) = 2:1. The Al\textsuperscript{3+}/Fe\textsuperscript{3+} ratio is changed in different molar ratios to prepare a series of ternary LDHs, so that the Mg/(Al + Fe) ratios were 10:4 + 1 (LDH A), 10:3 + 2 (LDH B), 10:2 + 3 (LDH C), and 10:1 + 4 (LDH D). The mixed-salt solutions were added to the solution of NaOH + Na\textsubscript{2}CO\textsubscript{3} (2 M) in a dropwise manner, maintaining the pH of 9.5. The obtained suspension was stirred using a magnetic stirrer at 300 rpm for 6 h at room temperature, then centrifuged, and washed thoroughly with deionized water to remove excess salt. Finally, the samples were dried overnight at 80 °C in a hot air oven.\textsuperscript{24}

\subsection*{2.3. Batch Mode Studies.} The adsorption experiments were done using a batch equilibration technique to study the effect of pH, contact time, and temperature on the sorption of MG by Mg/Al + Fe LDH. Weighed 1 g of MG was dissolved in 1 L of deionized water to obtain the stock MG solution. Various concentrations (100–2500 mg L\textsuperscript{-1}) of MG solution were freshly prepared from the stock solution.

To study the pH effect, 20 mL of 1000 mg L\textsuperscript{-1} of MG solution was poured into 100 mL of Erlenmeyer flasks with a stopper. The initial pH (4–9) of the MG solutions was adjusted by adding 0.01–1.0 M HCl or NaOH. An amount of 20 mg of adsorbent was added into the test solution at room temperature. For each experiment, the agitation time was fixed at 5 min. After agitation, the solution was centrifuged and the MG concentration analyzed in a JASCO 750 UV–vis spectrophotometer. The equilibrium adsorption capacity and the MG removal efficiency of Mg/(Al + Fe) LDH was estimated by using the mass balance eqs 1 and 2.

\begin{equation}
\% \text{ adsorbed} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\% \tag{1}
\end{equation}

\begin{equation}
q_e = \left( \frac{C_0 - C_e}{m} \right) \times V \tag{2}
\end{equation}

where $q_e$ is the adsorption capacity (mg g\textsuperscript{-1}), $C_0$ and $C_e$ are the equilibrium concentrations (mg L\textsuperscript{-1}) of MG at time t and the initial concentration, respectively, and m and V are the mass (mg) of the adsorbent and the volume (L) of solution, respectively.

The kinetic studies were examined by taking 20 mg of each adsorbent into 100 mL Erlenmeyer flasks, containing 20 mL of 1000 mg L\textsuperscript{-1} MG solution at pH 4, with a stopper and oscillating for varying time period from 5 to 40 min in a thermostated water bath at room temperature. The samples were centrifuged at specific time interval and the concentration of MG was analyzed by a UV–vis spectrophotometer. The obtained data were fitted to pseudo-first-order, pseudo-second-order, Elovich kinetic models, and intraparticle diffusion as shown in Table 1.

\begin{table}[h]
\centering
\caption{Kinetics Models Applied for MG Adsorption\textsuperscript{a}}
\begin{tabular}{|c|c|c|c|}
\hline
model & equation & parameters & reference \\
\hline
pseudo-first-order & $q_t = q_{eq}(1 - e^{-kt})$ & $q_{eq}, k_1$ & 25, 26 \\
pseudo-second-order & $q_t = \frac{k_2q_{eq}t}{1 + k_2q_{eq}t}$ & $k_2, q_{eq}$ & 25, 27 \\
intraparticle diffusion & $q_t = q_{dsf}F_s + l$ & $k_d, l$ & 28 \\
Elovich & $q_t = \frac{1}{\beta} \ln(a\beta) + \frac{1}{\beta} \ln t$ & $a, \beta$ & 29 \\
\hline
\end{tabular}
\textsuperscript{a} $q_{eq}$ is the quantity of the adsorbate adsorbed at equilibrium (mg g\textsuperscript{-1}); $q_t$ is the quantity of the adsorbate adsorbed at time t (mg g\textsuperscript{-1}); $k_1$ is the pseudo-first-order rate constant (min\textsuperscript{-1}); $k_2$ is the pseudo-second-order rate constant (g mg\textsuperscript{-1} min\textsuperscript{-1}); $k_d$ is the intraparticle diffusion rate constant (mg g\textsuperscript{-1} min\textsuperscript{-1}); l is a constant related to the boundary layer thickness; $a$ is the adsorption rate constant (mg g\textsuperscript{-1} min\textsuperscript{-1}); and $\beta$ is the desorption rate constant (g mg\textsuperscript{-1}).
\end{table}

The adsorption isotherms were investigated by changing the initial concentration of MG between 100 and 2500 mg L\textsuperscript{-1} at constant pH of 4. An amount of 20 mg of each sorbent was mixed with 20 mL of adsorbate solution and oscillated on a thermostated shaking water bath at temperatures 293, 303, 313, and 323 K for 5 min. The experimental adsorption equilibrium data were studied by two-parameter isotherms, such as Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models, and three-parameter isotherms, such as Sips, Toth, and Redlich–Peterson, and Khan models. The equations of the models are shown in Table 2.\textsuperscript{30–37} The thermodynamic parameters, such as the change in enthalpy ($\Delta H^\circ$), change in entropy ($\Delta S^\circ$), and change in free energy ($\Delta G^\circ$), were estimated from the considered temperature. To confirm the MG loading on the adsorbent, 50 mg of adsorbent was agitated in 50 mL of 1000 mg L\textsuperscript{-1} at pH 9 for 5 min in a thermostated water bath. The MG-loaded adsorbent was collected and dried in the oven for 8 h.

\subsection*{2.4. Zero Point Charge (pH\textsubscript{ZPC}).} If the pH was less than the pH\textsubscript{ZPC} value, there was the donation of more protons and the development of a positive charge on the surface of the
Table 2. Isotherm Models Used in the Study of MG Adsorption

| Model            | Equation                              | Parameters | Reference |
|------------------|---------------------------------------|------------|-----------|
| Langmuir         | $q_{eq} = \frac{q_m K C_{eq}}{1 + K C_{eq}}$ | $q_m, K$   | 30        |
| Freundlich       | $q_{eq} = K_C \frac{C_{eq}^{1/n}}{1 + K_C C_{eq}}$ | $K_C, n$   | 31        |
| Temkin           | $q_{eq} = \frac{RT K_T}{b_T} \ln(A_T C_{eq})$ | $b_T, A_T$ | 32        |
| Dubinin–Radushkevich | $q_{eq} = q_m e^{-\beta x}$ | $q_m, \beta$ | 33        |
| Sips             | $q_{eq} = \frac{q_m C_{eq}^{1/3}}{1 + b C_{eq}}$ | $q_m, b, n$ | 34        |
| Toth             | $q_{eq} = \frac{q_m C_{eq}}{(1 + a q_m C_{eq})^{2/n_T}}$ | $q_m, K_T, n_T$ | 35        |
| Redlich–Peterson | $q_{eq} = \frac{K_{BP} C_{eq}}{1 + a q_{BP} C_{eq}}$ | $K_{BP}, a_{BP}, g$ | 36        |
| Khan             | $q_{eq} = \frac{q_m b_T C_{eq}}{(1 + b_T C_{eq})^n}$ | $q_m, a_t, b_t$ | 37        |

$q_{eq}$ is the adsorption capacity (mg g$^{-1}$); $q_m$ is the maximum monolayer adsorption capacity (mg g$^{-1}$); $C_{eq}$ is the equilibrium concentration of adsorbate in the solution (mg L$^{-1}$); $b$ is the Langmuir adsorption constant (L mg$^{-1}$); $K_C$ is the Freundlich isotherm constant (mg g$^{-1}$); $n$ is the adsorption intensity; $A_T$ is the Temkin isotherm equilibrium binding constant (L g$^{-1}$); $b_T$ is the Temkin isotherm constant; $\beta$ is the Dubinin–Radushkevich isotherm constant (mol$^2$ kJ$^{-1}$); $K_T$ is the Toth isotherm constant (mg g$^{-1}$); $n_T$ is the Toth isotherm constant; $a_{BP}$ is the Redlich–Peterson isotherm constant; $K_{BP}$ is the Redlich–Peterson isotherm constant (L g$^{-1}$); $g$ is the Redlich–Peterson isotherm exponent; $b_t$ is the Khan isotherm constant; and $a_t$ is the Khan isotherm exponent.

The surface area of Mg/(Al + Fe) (10:2 + 3) LDH in 20 mL of 0.1 M NaCl solution was determined by a batch mode study. Initially, 20 mg of Mg/(Al + Fe) (10:2 + 3) LDH in 20 mL of 0.1 M NaCl solution was taken and the initial pH (pH$_I$) of NaCl solution was adjusted within the pH $\sim$ 0.5–7.5 by the addition of 0.1 M HCl and 0.1 M NH$_4$OH. The suspension was equilibrated at 25 °C for 24 h by stirring, was centrifuged, and the final pH value (pH$_F$) was determined. The procedure was repeated with 0.01 M NaCl solution. The pH$_ZPC$ value was calculated as 7.2 after a plot of pH$_I$ vs pH$_F$ values.

2.5. Physicochemical Characterization. The chemical composition of the prepared LDHs samples was obtained by atomic adsorption spectroscopy, and the water content was calculated using eq 3:

$$2 = 3n_c - n_i$$

where $n_c$ is the number of carbonate anions and $n_i$ is the number of interlayer water molecules per solid formula. The Brunauer–Emmett–Teller (BET) surface areas, average pore diameter, and pore volume of the prepared LDH samples were determined by multipoint N$_2$ adsorption–desorption method at the liquid N$_2$ temperature (77 K) by an ASAP 2020 (Micromeritics). The samples were degassed at 110 °C and 5 × 10$^{-4}$ Torr for 5 h to remove the physically adsorbed moisture. The powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX III VC diffractometer. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Varian FTIR spectrophotometer (FTS-800) at room temperature by taking KBr as the reference in the range of 400–4000 cm$^{-1}$. The adsorbate concentration analysis was done by using a UV–vis spectrophotometer of the V-750 JASCO model. Transmission electron microscopy (TEM) images were obtained on a Philips TECHNAI G2 operated at 200 kV, in which the samples were prepared by dispersing the powdered samples in ethanol by sonication for 15 min and then drop-drying on a copper grid coated with carbon film.

3. RESULTS AND DISCUSSION

3.1. Spectral Characterization. The N$_2$ sorption studies and the corresponding isotherms for the LDH A, LDH B, LDH C, and LDH D are shown in Figure 1. The sorption represents the aggregation of slitlike pores with platelike particles by following a type IV isotherm with a H3 hysteresis loop (IUPAC). The BET surface area values of the LDH A to LDH D are given in Table 3. As illustrated in Table 3, an increase in the molar content of iron from LDH A to LDH D leads to an increase in the specific surface area from 62 to 105 m$^2$ g$^{-1}$. The high surface area in the case of LDH D may be due to the deposition of aggregated amorphous Fe$_2$O$_3$ on the LDH surface. The increased iron amount promotes the formation of more active sites on the surface, favoring attractive sorption.

The X-ray diffraction patterns of the series of ternary Mg/Al + Fe-CO$_3$ LDH with different Al$^{3+}$/Fe$^{3+}$ molar ratios are shown in Figure 2. The presence of sharp and symmetric (003), (006), (009), (110), and (113) planes suggests a layered structure and signifies the hexagonal LDH in the 3R packing of octahedral symmetry. As the radius of Fe$^{3+}$ is more than that of Al$^{3+}$, the array density of the atoms on the surface sheet of Mg/Al + Fe-CO$_3$ LDH is smaller than that of the atoms at the surface of Mg/Al-CO$_3$ LDH. Therefore, from LDH A to LDH D, the...
position of the (110) crystal planes shifts to a lower $2\theta$ angle, indicating an isomorphous substitution of Al$^{3+}$ by Fe$^{3+}$. Although Mg/Al + Fe LDH brucite layer is stable, the incorporation of iron in the LDH crystal is restricted with increase in iron content. After a particular iron concentration, the excess unsubstituted iron is proposed to be present in the form of amorphous Fe$_2$O$_3$ in LDH D.42

**Figure 3** shows the transmission electron microscopy images of the hydrotalcite samples. The small irregular flakes like particles are shown in the image for LDH A. The particle size decreases upon the incorporation of iron into the brucite-like layers from LDH A to LDH D, from which we can also predict the growth of the amorphous Fe$_2$O$_3$ phase.

**3.2. Effect of Fe$^{3+}$ Substitution on MG Removal.** The removal efficiency of pure Mg/Al LDH (LDH X) is compared by varying the Al/Fe molar content onto the MG dye. As shown in **Figure 4**, the percentage of removal is increased with increasing order from LDH X to LDH C. The uptake percentage of MG is calculated to be 67 to 92 as iron loading increases. The percentage of MG removal follows the order LDH C > LDH B > LDH D > LDH A > LDH X. The highest removal efficiency is exhibited by LDH C (Al + Fe ratio 2:3), as the substitution of Fe$^{3+}$ with Al$^{3+}$ is optimal in the Mg/Al + Fe LDH sample. The enhanced activity of LDH C may be attributed to the fact that the electropositive character of transition metal Fe is more than that of Al and the incorporation of Fe in Mg/Al LDH creates a more positive charge on the surface of the ternary LDH, thus favoring adsorption. When the molar ratio of Al/Fe increases to 1:4, the agglomeration of Fe$_2$O$_3$ on the surface reduces the competence of dye adsorption (74%), as mentioned in XRD.43

**3.3. Effect of Initial pH.** The adsorption capacity and the removal of the dye from the aqueous solution are greatly

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**Table 3. Average Crystallite Size and BET Surface Area Values of Mg/Al + Fe LDH with Different Molar Ratios**

| Mg/Al + Fe LDH | molar ratio | chemical composition | avg size (nm) | BET surface area (m$^2$ g$^{-1}$) |
|---------------|-------------|----------------------|--------------|---------------------------------|
| LDH A         | 10:4 + 1    | Mg$_{65}$Al$_{12.7}$Fe$_{0.068}$(OH)$_2$(CO$_3$$^{2-}$)$_{0.17}$·1.49H$_2$O | 19.98        | 62                             |
| LDH B         | 10:3 + 2    | Mg$_{66}$Al$_{12.0}$Fe$_{0.13}$(OH)$_2$(CO$_3$$^{2-}$)$_{0.16}$·1.52H$_2$O | 21.9         | 83                             |
| LDH C         | 10:2 + 3    | Mg$_{65}$Al$_{12.0}$Fe$_{0.204}$(OH)$_2$(CO$_3$$^{2-}$)$_{0.16}$·1.52H$_2$O | 22.5         | 91                             |
| LDH D         | 10:1 + 4    | Mg$_{65}$Al$_{12.0}$Fe$_{0.273}$(OH)$_2$(CO$_3$$^{2-}$)$_{0.17}$·1.49H$_2$O | 22.7         | 105                            |

**Figure 2.** X-ray diffractograms of Mg/Al +Fe-CO$_3$ LDH with Al + Fe in different molar ratios.

**Figure 3.** TEM images of (A) LDH A, (B) LDH B, (C) LDH C, and (D) LDH D.
dependent on the pH of the solution, which affects the surface charge of the adsorbent and the degree of ionization of the dye molecule. At lower pH, the surface of the adsorbent gets protonated and attracts the positively charged dye molecules to the surface. At a higher pH, the surface groups get deprotonated and the adsorption proceeds through electrostatic attraction between the negatively charged surface and the positively charged dye cations. Moreover, at a lower pH, the H⁺ ions and positively charged dye molecules compete for appropriate adsorption sites on the surface of the catalyst. However, at a higher pH, the uptake of dye molecules increases.

The influence of initial pH on the adsorption of MG is carried out at various pH values by adjusting the pH to 3.9, 5.5, 7.57, and 9.5, as illustrated in Figure 5. It can be seen that the removal is 99% for the pH value of 7.5 and above for LDH C. At the pH value less than 7, the decrease in the adsorption may be attributed to two factors. (1) As the pH decreases, the number of positively charged adsorbents experience a force of repulsion on the positive surface of the adsorbent having the pH_{pzc} value 7.2. The cationic dye encounters competition with the protons and the adsorption of MG becomes restricted. (2) At a higher pH, the excess OH⁻ ions present in the solution get attached to the positively charged Mg/Al + Fe LDH and accumulate on the LDH surface to form a negative layer. As a result, the positively charged cationic dye MG molecules get tightly bound to the OH⁻ ion of LDH by the electrostatic force of attraction, as shown in Scheme 1. As the pKₐ value of MG is 10.3, it exhibits excellent adsorption at a higher pH value.45

3.4. Effect of Contact Time. For dye uptake, the contact time plays an important role, as the adsorbate species diffuse from bulk to active sites of the surface. To determine the relationship between the MG removal and contact time, a series of systematic experiments are performed taking 1000 mg/L⁻¹ MG solution over a period of 40 min at pH 4. As displayed in Figure 6, it is observed that the adsorption rate of MG is significantly more at the initial stage due to the abundant availability of active sites. The MG molecules easily gain accessibility to the sites and in the first 5 min, the adsorption reaches (63.3%) the maximum for LDH C. Subsequently, the steric hindrance caused by the bulky MG dye molecules on the surface hinders the tempo of adsorption, reaching a state of equilibrium (95.32%) after 20 min. Figure 4 demonstrates the highest uptake of MG by LDH C, which is 63.3% in the first 5 min and 99.04% after 25 min. This is due to the high surface area of LDH C.

As displayed in Figure 7, the absorbance of MG dye decreases with increase in time (for t values 0 and 20 min, A is 1.57 and 0.01, respectively), indicating an efficient removal of the dye by ternary LDH C.

3.5. Adsorption Kinetics. To explain the transport of MG on to Mg/Al + Fe LDH and to determine the rate of adsorption and the dynamics involved during adsorption, the Lagergren pseudo-first-order,25,26 pseudo-second-order,27 intraparticle diffusion model,28 and Elovich models29 are applied to the experimental data from the effect of contact time for all of the Mg/Al + Fe LDH samples. The nonlinear equations for these models are given in Table 1. The kinetics parameters of all the models got from the adsorption experimental data obtained for LDH A, LDH B, LDH C, and LDH D is represented in Table 4. The reliance of the model that best fits the experimental data is chosen based on the lowest sum of squared residuals (SSR).46 It is observed that the obtained data best fit the pseudo-second-order model. So, the adsorption of MG on LDH occurs through bimolecular interactions involving the sharing or exchange of electron.

To further describe the rate-limiting step, the intraparticle diffusion model and the kinetics are studied. Generally, adsorption occurs through four processes. (1) Adsorbates are transmitted from the bulk phase onto the adsorbent surface. (2) The transport of incoming adsorbate passes through the liquid film attached to the adsorbent surface (film diffusion). (3) The adsorbate is passed within the pores of the adsorbent (intraparticle diffusion). (4) There is an interaction between the active site of the adsorbent and adsorbate.30 As the plot obtained from the q_{t} versus t^{1/2} does not pass through the origin, it suggests that the intraparticle diffusion partially controls the rate-limiting step and the adsorption of MG proceeds by film diffusion process as described above.48—50 The intraparticle diffusion constant (k_{d}) is obtained from the plot and increases from LDH A to LDH C and then further decreases for LDH D. The formation of Fe₂O₃ on the LDH surface may restrict the transportation of MG to the external surface of the adsorbent. Therefore, a higher adsorption capacity (q_{e}) is obtained for LDH C (Table 5).

3.6. Effect of Temperature. The solution temperature greatly affects the removal efficiency of MG. This may be due to the textural properties of the adsorbents, decrease in the viscosity of the solution, and increase in the rate of diffusion of
the adsorbent.\textsuperscript{46,51,52} The effect of temperature is investigated over the temperature range of 293–323 K for all of the adsorbents as shown in Figure 8. With an increase in adsorbate temperature, the adsorption capacity ($q_e$) is increased for all of the samples. In this case, the high uptake of MG is due to the decrease in the viscosity of the solution, faster mobility of MG toward the active sites, an increase in the porosity and pore volumes of the adsorbent resulting in the enhancement of active sites.\textsuperscript{46,51,52} That is why, the effective removal of MG is carried out.

3.7. Adsorption Isotherm and Modeling. Adsorption isotherms usually play a vital role in predicting the mechanism of how the MG molecules interact with the active sites on the adsorbent surface. The two-parameter isotherms, such as Langmuir,\textsuperscript{30} Freundlich,\textsuperscript{31} Temkin,\textsuperscript{32} and Dubinin−Radushkevich,\textsuperscript{33} and three-parameter isotherms, such as Sips,\textsuperscript{34} Khan,\textsuperscript{37} Redlich−Peterson,\textsuperscript{36} and Toth,\textsuperscript{35} are applied to understand the fitted model. All of the nonlinear isotherms mentioned above are given in Table 3. The experimental adsorption equilibrium data for the adsorbents are calculated by the initial MG concentration over the temperature range of 293–323 K. The acceptability of the models that best fit the equilibrium data is considered from the lowest sum of the squared residuals (SSR).\textsuperscript{46} The values of different parameters obtained during MG adsorption for the fitted model are presented in Table 5.

Table 5 shows that the Freundlich isotherm can only best fit to the experimental data obtained for LDH A, LDH B, LDH C, and LDH D, as shown in Figure 9. The curves for best-fit isotherm model for different adsorbent are shown. The Freundlich isotherm model may assume the heterogeneity of the adsorbent surface.\textsuperscript{53} Therefore, MG adsorption onto LDH A, LDH B, LDH C, and LDH D might be assumed to be a multilayered adsorption. From Table 5, it is observed that the $K_F$ value decreases with increase in temperature (in order following LDH C > LDH B > LDH D > LDH A at temperature 293 K, 303 K, 313 K and 323 K). Hence, the highest $K_F$ value 21.43 is obtained for LDH C at 293 K. The Freundlich constant $n$ values (1.59–2.21) are ≤10, indicating that MG adsorption is favorable.\textsuperscript{46,53}

The Langmuir maximum adsorption capacity ($q_m$) is varied from 80.50 to 484.52 for LDH A, 997.50 to 820.65 for LDH B, 1072.82 to 1045.90 for LDH C, and 551.15 to 458.02 for LDH D over the temperature range 293–323. This indicates the decrease in $q_m$ value with increase in temperature. The nature and shape of adsorption also depend on the value of the separation factor ($R_L$) as expressed in eq 4.
where \( b \) is the Langmuir isotherm constant obtained from Table 5. \( C_i \) is the initial MG concentration. Adsorption is expected to be favorable if \( 0 < R_L < 1 \), unfavorable if \( R_L > 1 \), irreversible if \( R_L = 0 \), and linear if \( R_L = 1 \). All of the \( R_L \) values are calculated to lie in the range of \( 0 < R_L < 1 \). Hence, it indicates a favorable adsorption of MG dye on LDH adsorbent.\(^{46,54}\)

Figure 8. Effect of temperature on the MG adsorption onto (a) LDH A, (b) LDH B, (c) LDH C, and (d) LDH D (condition: 20 mL of 100–2500 mg L\(^{-1}\) MG solution, pH = 4, 20 mg of adsorbent, 5 min).

The Langmuir maximum adsorption capacity \( (q_m = 1072.82 \text{ mg g}^{-1}) \) for MG is compared with other reported values for different adsorbents. It is found superior than other adsorbent in terms of MG removal. The result shows that Mg/Al + Fe LDH is a super and smart adsorbent of MG (Table 6).

3.8. Thermodynamic Studies. The adsorption process is accompanied by the thermodynamic parameters, such as change in enthalpy \((\Delta H^o)\), change in entropy \((\Delta S^o)\), and change in Gibbs energy \((\Delta G^o)\), as it is temperature dependent. To examine the feasibility and spontaneity of the adsorption process, the thermodynamic parameters are calculated.
process, ΔG values are considered. If ΔG is negative, the process is spontaneous. From the qe value obtained over the studied temperature, we can assume that the reaction is either endothermic or exothermic. The adsorption process is endothermic if the adsorption capacity (qeq) increases with increase in temperature, and the condition is reversed for the exothermic process. The following parameters are assessed from eqs 5, 6, and 7:

\[ K_c = \frac{C_{\text{ad}}}{C_e} \quad (5) \]

\[ \Delta G^\circ = -RT \ln K_c \quad (6) \]

\[ \ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (7) \]

where \( K_c \) is the thermodynamic equilibrium constant, \( C_{\text{ad}} \) (mg L\(^{-1}\)) is the equilibrium concentration of adsorbate onto adsorbent surface, and \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration in an aqueous solution. \( \Delta G^\circ \) (kJ mol\(^{-1}\)) is the standard Gibbs energy change. \( T \) (K) is the temperature in Kelvin, \( R \) is the gas constant (8.314 J (mol K\(^{-1}\))), \( \Delta H^\circ \) (kJ mol\(^{-1}\)) is the enthalpy change, and \( \Delta S^\circ \) (J (mol K\(^{-1}\))) is the entropy change. The values of the change in enthalpy (\( \Delta H^\circ \)) and entropy (\( \Delta S^\circ \)) are obtained from the slope and intercept found from the plot of ln \( K \) against 1/\( T \), respectively.

From Figure 10 and Table 7, we observe that the negative values for \( \Delta G^\circ \) suggest that MG adsorption on the adsorbents is a spontaneous and feasible process. Further, it is noticed that there is a decrease in the negative value for \( \Delta G^\circ \), which is obtained with the rise in temperature, suggesting a better adsorption at a lower temperature. An exothermic process of adsorption is confirmed from the negative \( \Delta H^\circ \) values; in addition, a decrease in the disorderness at the solid–solution interface is predicted from a negative \( \Delta S^\circ \) value. Hence, the adsorption of MG on different LDH is typically an enthalpy-driven process.

From the value of heat of adsorption, the interaction between the adsorbent and adsorbate can be determined. If the \( \Delta H \) value lies in the range 2.1–20.9 kJ mol\(^{-1}\), the interaction is assumed to be physical (physisorption). However, it is termed chemisorption if \( \Delta H \) lies between 80 and 200 kJ mol\(^{-1}\). Because the \( \Delta H \) values obtained lie within 20.9, the process of removal of MG from the aqueous solution by using LDH A, LDH B, LDH C, and LDH D is assumed to be physisorption (van der Waals forces).

Thus, establishing LDH C with an optimum iron content as a super and smart adsorbent. To know the successful adsorption of MG on LDH C, we carried out the XRD, FTIR and UV–vis spectra for LDH C and MG-loaded LDH C.

### 4. CHARACTERIZATION OF MG-LOADED LDH

#### 4.1. XRD Spectral Analysis.

As shown in Figure 11, the XRD patterns clearly indicate that the characteristic XRD peak
of LDH C is maintained even after the adsorption of malachite green. Reduction in the intensity of LDH C after adsorption (MG-loaded LDH C) indicates a decrease in the degree of crystallinity.

4.2. FTIR Spectral Analysis. The FTIR spectra of LDH C and malachite green-loaded LDH C can be used as an appropriate technique for the survey of dye loading on Mg/Al + Fe LDH. As shown in Figure 12, the broad absorption band in the region of 3417 cm⁻¹ is assigned to the O−H stretching vibrational mode of the hydroxyl groups in the LDH and the interlayer water molecules.⁶⁴ The medium band close to 1640 cm⁻¹ is attributed to the bending vibration of the stretched water molecules.⁶⁵ The bands at 1390 and 870 cm⁻¹ are due to carbonate.⁶⁶ The absorption peak at 585 cm⁻¹ confirms the formation of α-Fe₂O₃. This has been ascribed as after the complete substitution of Fe³⁺ in the brucite layer of hydrotalcite

Table 6. Comparison of Langmuir Maximum Capacity (qₘ) for the MG Adsorption on Ternary LDH

| adsorbent               | condition                                      | qₘ (mg g⁻¹) | reference |
|------------------------|------------------------------------------------|-------------|-----------|
| PE-ABR                 | 100 mg L⁻¹, 4 g L⁻¹ dose, 24 h, 25 °C           | 89.05       | 55        |
| CuO-NP-AC              | pH 6.0, 20 mg L⁻¹, 20 mg dose, 5 min, 25 °C     | 87.71       | 56        |
| 3A zeolite             | pH 7, 10 mg L⁻¹, 0.1 g dose, 30 min             | 47.17       | 57        |
| Mg/Fe-CLDH             | pH 8, 20–160 mg L⁻¹, 0.08 g L⁻¹ dose, 60 min, 25 °C | 656.88      | 58        |
| fibrous cellulose sulphate | 200 mg L⁻¹, 0.2 g L⁻¹, 30 min, 25 °C               | 960         | 59        |
| WHPA–OMCNT             | pH 6, 40–800 mg L⁻¹, 4 mg dose, 120 min, 25 °C | 840.3       | 60        |
| Mg/(Al + Fe) (10:4 + 1) LDH | pH 4, 100–2500 mg L⁻¹, 20 mg of dose, 5 min, 20 °C | 580.50      | this study |
| Mg/(Al + Fe) (10:3 + 2) LDH | pH 4, 100–2500 mg L⁻¹, 20 mg of dose, 5 min, 20 °C | 997.50      | this study |
| Mg/(Al + Fe) (10:2 + 3) LDH | pH 4, 100–2500 mg L⁻¹, 20 mg of dose, 5 min, 20 °C | 1072.82     | this study |
| Mg/(Al + Fe) (10:1 + 4) LDH | pH 4, 100–2500 mg L⁻¹, 20 mg of dose, 5 min, 20 °C | 551.15      | this study |

Table 7. Thermodynamic Parameters for the Adsorption of MG on LDH A, LDH B, LDH C, and LDH D

| adsorbent | ΔH (kJ mol⁻¹) | ΔS (J mol⁻¹ K⁻¹) | ΔG (kJ mol⁻¹) |
|-----------|--------------|-----------------|--------------|
|           |              |                 | 293 K        | 303 K        | 313 K        | 323 K        |
| LDH A     | −11.216      | −43.149         | −2.231       | −1.891       | −1.325       | −1.219       |
| LDH B     | −19.393      | −85.869         | −2.170       | −1.551       | −0.867       | −0.840       |
| LDH C     | −11.046      | −40.788         | −0.668       | −0.395       | −0.027       | −0.011       |
| LDH D     | −1.194       | −34.636         | −2.597       | −2.495       | −2.112       | −1.998       |

Figure 9. Fitted Langmuir and Freundlich isotherm at different temperatures for (a) LDH A, (b) LDH B, (c) LDH C, and (d) LDH D (condition: 20 mL of 100–2500 mg L⁻¹ MG solution, pH 4, 20 mg of adsorbent, 5 min).
maintaining the stability of Fe-LDH by $M^{2+}/M^{3+} = 2$, the excess unsubstituted Fe$^{3+}$ has been present in the form of Fe$_2$O$_3$. The finger print peak for MG between 1500 and 500 cm$^{-1}$ supports the peak at 1590.77 cm$^{-1}$, matching the C=C stretching of benzene ring. The peak between 1200 and 1142 cm$^{-1}$ is for the C-N stretching vibration of the aromatic ring. The peak for $\text{-CH}_2$ scissoring, $\text{-CH}_3$ asymmetric band, and $\text{-NH}_2$ wag are observed at 1434, 1370, and 827 cm$^{-1}$, respectively. From the above observation, it is concluded that MG is successfully adsorbed on LDH C.

4.3. UV–Vis Spectral Analysis. Figure 13 compares the UV–vis diffusion reflectance spectra of LDH C before and after adsorption. The strong adsorption band at 254 nm shows the presence of the Fe$^{3+}$ species. The adsorption wavelength 621 nm confirms the adsorption of malachite green on the LDH surface.

5. ADSORPTION MECHANISM AND RECYCLE PERFORMANCE

The possible mechanism for cationic MG dye adsorption by anionic clay Mg/Al + Fe LDH based on the above observations may be described as follows (Scheme 2).

Case 1: As MG is a cationic aromatic azo dye, the delocalized "$\pi$" electrons in the aromatic ring form a negative charge cloud. The negative charge is attracted by the positively charge surface.
of Mg/Al + Fe LDH through an electrostatic force of attraction.68

Case 2: Another reason for adsorption is the direct interaction between the positively charged azo group of MG with the negative interlayer anions (CO$_3^{2-}$) group of the LDH. It is very important to study the stability and reusability of an adsorbent to achieve economic viability and efficiency, the same adsorbent is used for various runs. After three cycles of experiment, it is found that the ternary LDH Mg/(Al + Fe) still removes more than 90% of the dye within a time span of 30 min, as shown in Figure 14. The adsorbed dye is thoroughly washed with ethanol and deionized water, and the adsorbent is dried under hot air oven at 100 °C for 6 h and subjected to dye removal. The color and morphology undergo no change during the cycle experiments, establishing the stability and efficiency of the material for reuse.

6. CONCLUSIONS

A ternary layered double hydroxide doped with Fe$^{3+}$ ions in the octahedral sites of Mg/Al LDH brucite layer was prepared by the co-precipitation method, and the adsorption of MG from the aqueous solution was proficiently carried out on it. It was observed that the adsorption capacity of the adsorbents significantly increased from 580.50 to 1072.82 mg g$^{-1}$ with increase in the iron content for Al + Fe molar ratio 4 + 1 to 2 + 3 except for the molar ratio 1 + 4, i.e., 551.15 mg g$^{-1}$ in 5 min. It was revealed that the incorporation of iron content on Mg/Al LDH surface could enhance the surface area, but the adsorption capacity was further decreased due to the agglomeration of Fe$_2$O$_3$ on the Mg/Al LDH surface. Hence, the highest adsorption capacity was achieved with Mg/(Al + Fe) with the molar ratio 10:2 + 3. The optimum removal of MG was noticed at pH 9, i.e., 99.94%, and the equilibrium was attained after 25 min. The adsorption followed the pseudo-second-order kinetics model specifying a bimolecular rate determination. From the applied isotherm model, Langmuir and Freundlich model were fitted well to the equilibrium data, but Freundlich model was best fitted, indicating a multilayered adsorption of MG on a heterogeneous adsorbent surface. The high adsorption capacity observed near ambient temperature favors
the treatment of effluents from several sources. The adsorption onto all of the adsorbent was spontaneous, feasible enthalpy driven, and exothermic in nature. The desorption experiment revealed that the adsorbents were efficiently regenerated. Even after 3 cycles, more than 90% of the MG can be removed. Thus, these adsorbents can be used as potential sorbents for reuse and do not produce secondary pollutant. Fast and efficient removal of malachite green by the MG/Al + Fe LDH may be due to the electrostatic interaction between (i) the positive LDH surface and the delocalized π electrons in the aromatic ring of azo dye and (ii) the cationic MG dye, OH⁻ ion, and the CO₃²⁻ group of the LDH.

The positive charge of LDH with a large surface area, abundant active sites, and compatibility made the sorbent a champion in water remediation. The present call for speed over quality and quantity for pollution remediation is very much satisfied by the ternary LDH, which can be used as a super and smart adsorbent in the future for the removal of dyes from water.

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**Notes**

The authors declare no competing financial interest.

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