Chapter- 3

Synthesis of Ternary Layered Double Hydroxides and their Application for Wastewater Treatment

3.1. Abstract

This study systematically investigates the optimisation of synthesis parameters for ternary layered double hydroxide (LDH) to achieve a pure phase and high crystallinity. The $[\mathrm{Co}^{2+}_{0.5}\mathrm{Al}^{3+}_{0.25}\mathrm{Fe}^{3+}_{0.25}(\mathrm{OH})_2].(\mathrm{CO}_3^{2-})_{0.125}.\mathrm{H_2O}$ or $\mathrm{CoAlFe}-\mathrm{CO}_3$ LDH is synthesised using the co-precipitation method and applied for wastewater treatment. The ternary LDH is synthesised at 60°C for 24 hours and exhibited maximum crystallinity with a crystallite size of 4 nm. The crystallinity index (CI) is a quantitative indicator of crystallinity, calculated using the x-ray diffraction (XRD) method. The influence of reaction time on the structural characteristics of this LDH was thoroughly investigated, mainly focusing on achieving well-crystalline LDH. Experimental results revealed a direct correlation between reaction time and crystallinity. This study highlights the significant influence of controlled synthesis and reaction time on producing high crystalline ternary LDH. The role of different parameters, such as solution pH, adsorbent dosage, contact time, and dye concentration, has been investigated. The adsorption isotherm data is analysed using different isotherm models, which shows this material having a significant adsorption capacity of 82.92 mg/g for Congo Red dye.

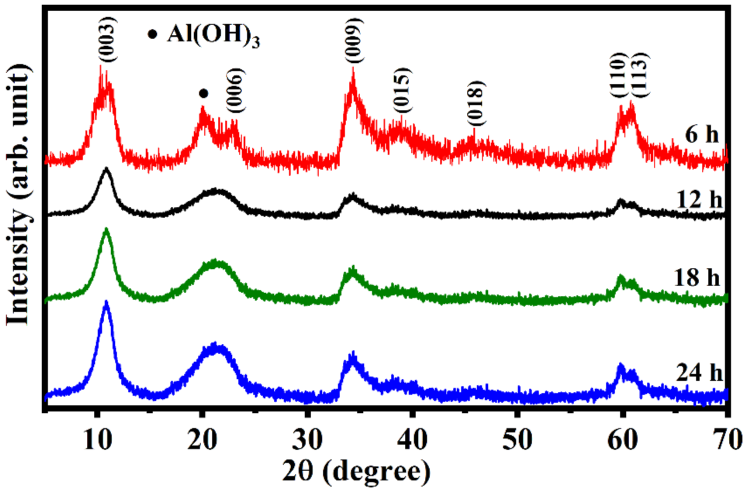

Figure 3.1: X-ray diffraction pattern of CoAlFe-CO_3 (6 h, 12 h, 18 h & 24 h).

3.2. Result and discussion

3.2.1. X-ray Diffraction Analysis

The synthesis processes of layered double hydroxides have been carefully curated to optimise the parameters to obtain pure-phase LDH with high crystallinity. The XRD pattern of CoAlFe (6 h, 12 h, 18 h, 24 h) LDH is presented in Figure 3.1. As shown in Figure 3.1, the most intense diffraction peaks at $2\theta = 10.96°$, 23.06°, and 34.18° belong to basal planes (003), (006) and (009), respectively. Other peaks at $2\theta = 38.65°$, 45.35°, 59.70°, and 60.35° belonging to the (015), (018), (110), and (113) non-basal planes, respectively [146]. As the XRD shows, during the initial material synthesis for 6 hours at 60°C, an additional phase corresponding to the peak characteristics of aluminium hydroxides (JCPDS Card No. 37-1377) was observed at $2\theta = 20.06$ °. The subsequent increase in the reaction time to 12 hours, 18 hours and 24 hours at constant temperature resulted in the forming of a single phase and improved crystallinity (Table 3.1). The pure phase of LDH, having high crystallinity, was obtained for the extended reaction time of 24 hours at 60 °C. This result indicates that the synthesised LDH have a well-crystalline layered structure.

3.2.2. Crystallinity index (CI):

The Crystallinity Index (CI), indicating the volume fraction of crystallinity of a particular phase in a sample, acts as a quantitative indicator of crystallinity [147]. It reflects the average crystallite size, the degree of perfection, and the ordering within a crystal [148]. In this study, CI is calculated using XRD data. These results show that as ageing time increases, the CI also rises, which is associated with crystallite size. The crystal size and crystallinity index (CI) shown for different ageing times are shown in Table 3.1.

Table 3.1: A list of (003) peak position, full width at half maxima and crystallite size for the ternary layered double hydroxide.

Sample Name	Aging time	FWHM of reflected 003 plane (radian)	Crystallite size (nm)	Crystallinity index (CI)
CoAlFe LDH	6 h	0.0464	3	0.5010
	12 h	0.0436	3	0.6623
	18 h	0.0417	3	0.6631
	24 h	0.0361	4	0.6642

3.2.3. Role of reaction time for synthesis of layered double hydroxide

The reaction time is directly correlated with the obtained LDH's crystallinity. The FWHM decreases with the increase in reaction time (Table 3.1). The sharp basal peak (003) for the CoAlFe LDH, leads to a smaller FWHM, signifying a well-defined and highly crystalline structure in the material. The crystallite sizes are calculated using the Debye-Scherrer method. These findings demonstrate the significance of the synthesis process's reaction time as a crucial factor for obtaining crystalline LDH, potentially attributed to the extended duration of nucleation and crystal growth. The Debye-Scherrer equation determines the crystallite size [149]. The equation to determine the crystallite size from FWHM is given as,

$$D = \left(\frac{k\lambda}{\beta\cos\theta}\right) \qquad (3)$$

where D is the size of the particle, k is known as the Scherrer's constant (k= 0.94), λ is the x-ray wavelength (1.54178 Å), β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the angle of diffraction. The crystallite size for the basal (003) plane in all the prepared materials is 3 to 4 nm (Table 3.1).

3.2.4. Transmission Electron Microscopy (TEM) Analysis

The TEM analysis was used to investigate the morphology of the LDH, and the resulting TEM micrographs are presented in Figure 3.2. This LDH shows that the prepared material has a lamellar arrangement like previous reports [150]. Simultaneous nucleation and ageing in the presence of NaOH usually lead to agglomeration during the synthesis of LDHs through the co-precipitation technique [151].

The TEM images show agglomeration of the LDH particles. This phenomenon is primarily attributed to the smaller size of LDH particles, which results in a higher surface energy. To minimise this energy, the particles exhibit a tendency to

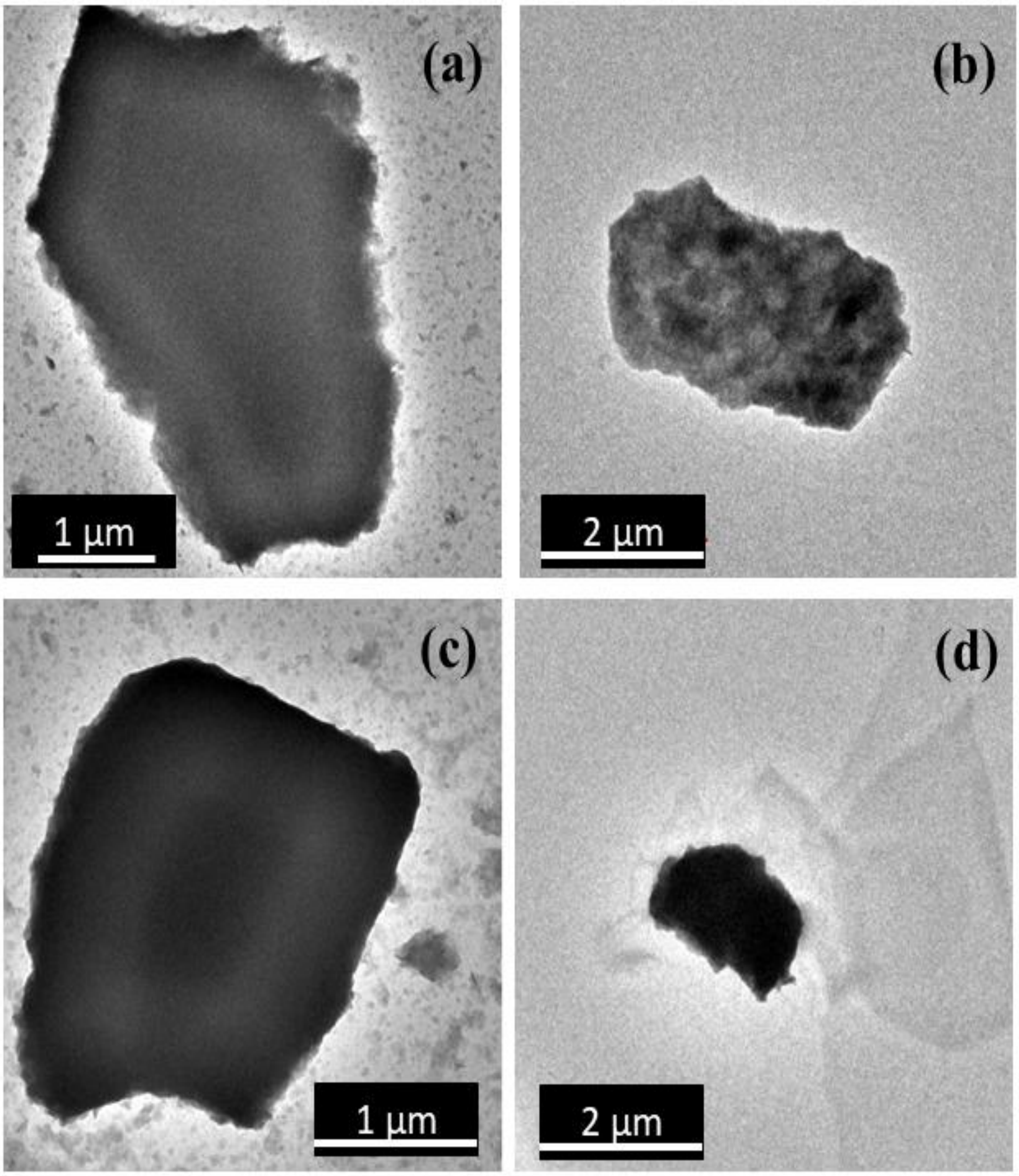

Figure 3.2: TEM Images of (a) CoAlFe-CO_3 (6 h) (b) CoAlFe-CO_3 (12 h), (c) CoAlFe-CO_3 (18 h), (d) CoAlFe-CO_3 (24 h).

agglomerate [152]. Furthermore, the coprecipitation technique is an inexpensive and facile method for nanoparticle synthesis, but it often leads to agglomeration of the nanoparticles, which is also the case regarding the CoAlFe LDH [153].

However, in co-precipitation reactions, the formation of LDHs does not occur immediately. Mixing time and induction time play a crucial role in forming the pure phase of LDHs. This phenomenon is conceivably attributed to the thorough diffusion of guest cations within the unoccupied lattice sites of the brucite-like layers or their substitution with host counterparts, which occurs predominantly at extended reaction durations [153,154].

3.2.5. Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The Fourier Transformed Infrared Spectroscopy (FTIR) spectra of the materials are shown in Figure 3.3. The hydrotalcite structure can be identified by three characteristic vibration bands associated with hydroxyl groups, octahedral layers, and interlayer species [146]. In Figure 3.3, the characteristic bands appear in similar positions for all the as-synthesized CoAlFe LDH. The broad and highly intense band around 3406 cm^{-1} can be ascribed to the symmetric and asymmetric stretching mode of the O – H bonds due to the presence of interlayer water molecules and O – H bonds attached to the cations in the layers or due to structural hydroxyl bonds. The band around at 2977 and 1628 cm^{-1} were identified as the water deformation $\delta(H_2O)$ and around 1340

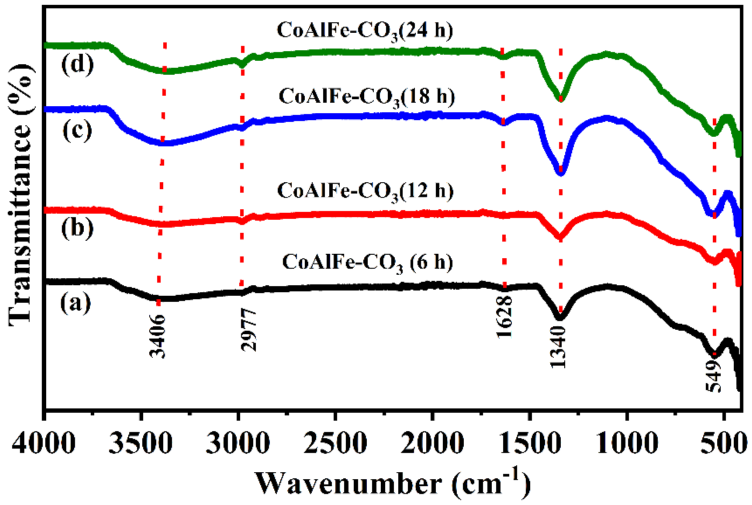

Figure 3.3: FTIR spectra of (a) CoAlFe-CO_3 (6 h), (b) CoAlFe-CO_3 (12 h) (c) CoAlFe-CO_3 (18 h) (d) CoAlFe-CO_3 (24 h).

cm^{-1} represent the ν_3 asymmetric stretching of the CO_3 anions in the interlayers respectively [155,156]. The band in the lower frequency range of 500 to 1000 cm^{-1} defines the formation lattice vibration mode of $M-O, M-OH, M-O-M$ (M = Co, Al, Fe) [157,158]. FTIR results verified the successful preparation of the ternary layered double hydroxide.

3.3. Kinetic studies

3.3.1. Effect of solution pH

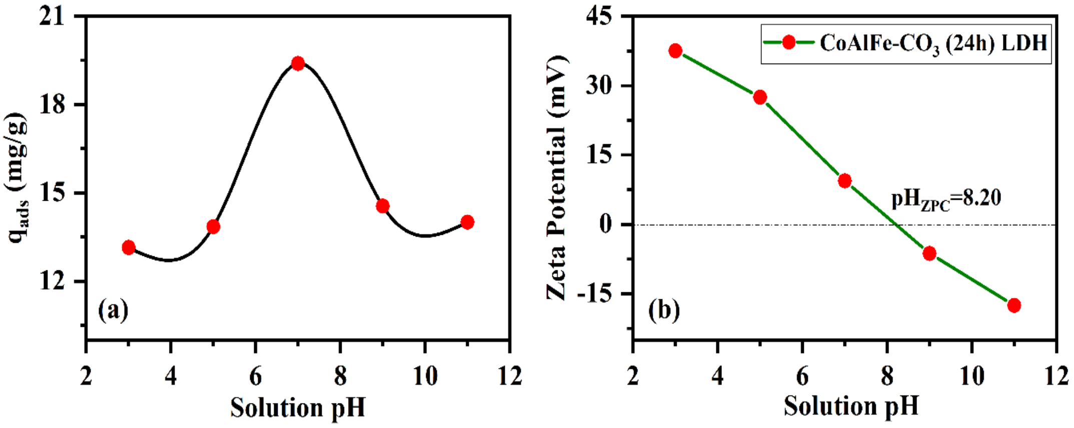

Figure 3.4: (a) Effect of solution pH in adsorption of Congo-red on to the CoAlFe-CO_3 (24 h) LDH, dot indicates the q_{ads} (b) Zeta potential, dot indicates the Zeta Potential value.

The solution pH is one of the crucial parameters for dye adsorption, as shown in Figure 3.4. CR is an anionic dye, so the solution pH is also a primary factor for adsorption. Primarily, the impact was observed when the pH of the solution shifted towards acidic or alkaline conditions. Figure 3.4 illustrates the impact of solution pH and zeta potential on the adsorption capacity of CR by the LDH. The removal efficiency increased with increasing the pH from 3 to 5, and the maximum adsorption was achieved at pH 7; next, in the alkaline medium, the removal capacity was decreased. The surface charge on the material can explain this phenomenon. At pH 3, the surface charge is positive but diminishes as the pH increases. The pH_{zpc} of the material is 8.20. Beyond this value, the surface becomes negatively charged, reducing its adsorption capacity. Although the surface is highly positive at pH 3, which is 37.5, the structure may be affected, resulting in much lower adsorption capacity than at pH 7, where the structure remains unaffected. This phenomenon can be attributed to the presence of CR predominantly in its anionic form at pH levels above 5.5, which enhances its affinity for the positively charged LDH through electrostatic interactions. The deprotonation of OH^- ions on the surface of the LDH results in an excess of OH^- in the alkaline medium, which causes repulsion with negatively charged dye and decreases dye adsorption capacity in the alkaline medium. Therefore, the dye removal occurred under a standard pH condition, specifically at a pH 7 [159,160].

3.3.2. Effect of contact time on congo-red adsorption

The effect of contact time is one of the critical parameters of the adsorption process. The amount of Congo-red was removed by CoAlFe LDH as a function of solid-liquid contact time, using as an adsorbent 50 mg with varied initial concentrations of 25-75 mg/L, is shown in Figure 3.5. The availability of the adsorbent active sites results in rapid CR removal at the reaction's earliest stages (10-60 min). With the increase in contact time, the saturation of active sites increases, resulting in a slow uptake capacity of CR with time. The kinetic study of CR adsorption shows that the removal equilibrium is reached after 120 min for all concentrations of CR.

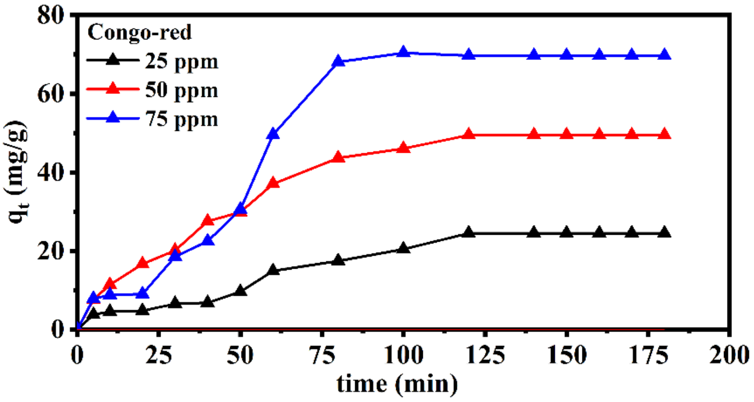

Figure 3.5: Effect of contact time and CR concentration in the adsorption of Congo-red onto the CoAlFe-CO_3 (24 h) LDH (ppm=mg/L).

3.3.3. Effect of Congo-red concentration

The congo-red dye concentration has an important role in the adsorption process. The amount of the dye adsorbed from 24.49 mg/L to 70.5 mg/L is shown in Table 3.2. The calculated removal CR percentages decreased from 97.96 to 94 % with increasing dye concentration from 25 to 75 mg/L. The higher uptake capacity of CR with lower concentration can be explained. The availability of the adsorption active sites is fixed, the adsorbent adsorbed the same amount of adsorbate. At higher CR concentrations, the ratio between the active sites of the material and the surface area decreases. Therefore, the removal percentages decrease with increasing the dye concentration [161].

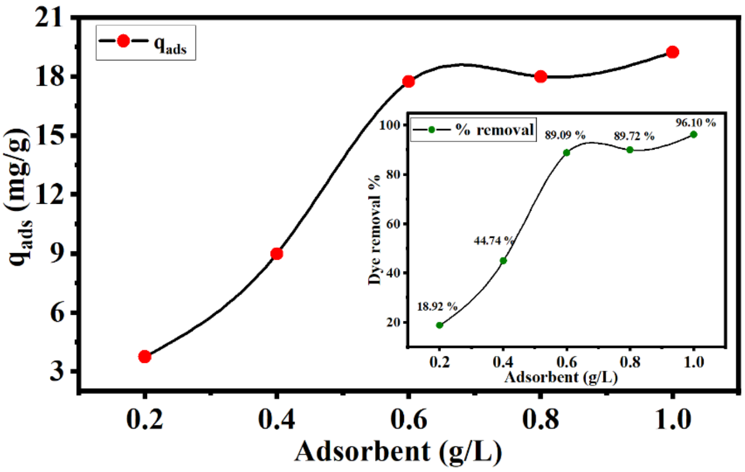

Figure 3.6: Effect of adsorbent dose in the Congo-red adsorption on CoAlFe-CO_3 (24 h) LDH, adsorbent mass =25 mg, V=25 ml, C_0= 20 mg/L, red dots indicate the q_{ads} and green dots indicates the removal efficiency.

3.3.4. Effects of adsorbent dosage

The quantity of the adsorbent employed directly influences the adsorption process. Figure 3.6 shows the effect of adsorbent dosages and removal percentage with variations in the amount of adsorbent. The percentage removal of Congo-red increases from 18.92 % to 96.10 % with the increase in the adsorbent from 0.2 g/L to 1 g/L, as shown in Figure 3.6. A higher uptake capacity was observed at a 1 g/L adsorbent dose due to more active sites in the material. Consequently, every type of active site on the adsorbent surface is fully exposed, making CR molecules easier to reach [162].

3.3.5. Kinetics model

Various models can be used to discuss the mechanism of solid-liquid interaction during adsorption. Several kinetics models were used to discuss the experimental data's mechanism and examine the adsorption process's controlling mechanism, such as

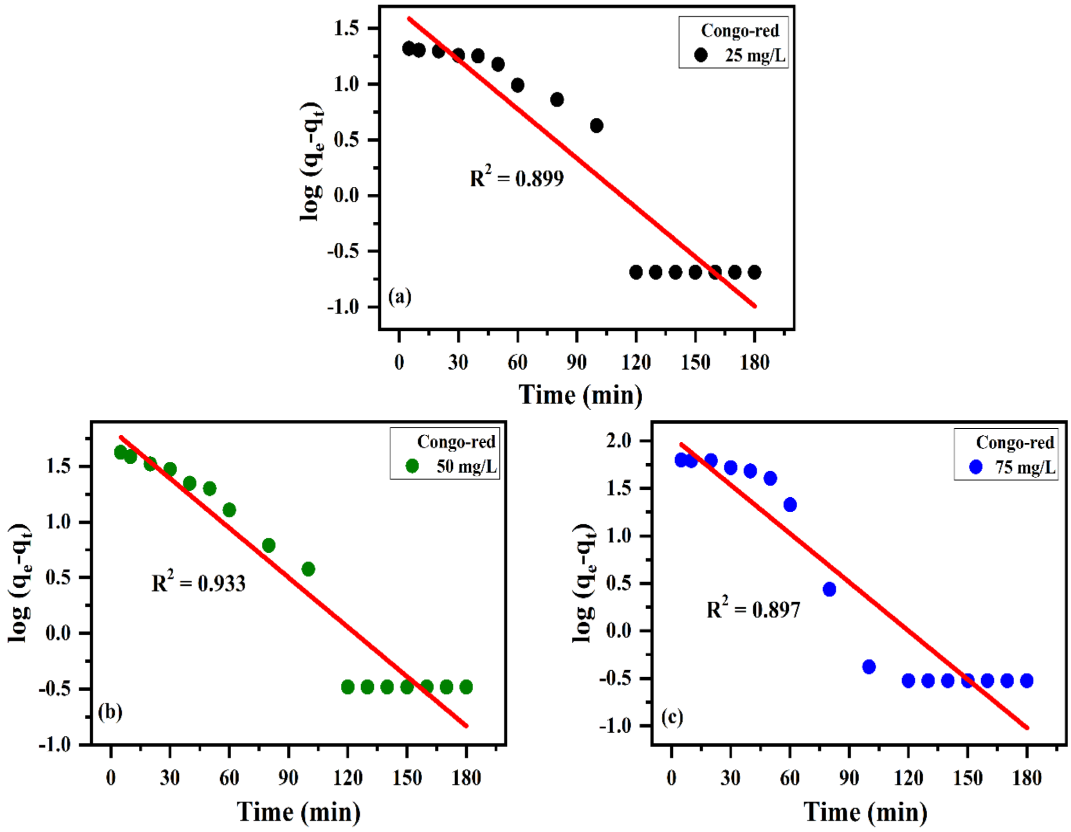

Figure 3.7: Pseudo-first-order kinetic model for CR concentration of (a) 25 mg/L (b) 50 mg/L (c) 75 mg/L, where the red line indicates the fitting and the dot indicates $log\ (q_e - q_t)$ value R^2 is the correlation coefficient (not applicable for low R^2 value).

chemical reaction, diffusion control, and mass transfer. In this study, the experimental data of CR adsorption by the LDH with varying dye concentrations from 25 to 75 mg/L was fitted using three kinetics models: pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

3.3.5.1. Pseudo-first-order and pseudo-second-order models

Figure 3.8 represents the pseudo-second-order kinetic model. The linear equation plot for the pseudo-first-order (Figure 3.7) kinetic model is derived as follows:

$$log\ (q_e - q_t) = log q_e - k_1 t \ \ .... (5)$$

Where q_e (mg/g) and q_t(mg/g) are the maximum adsorption capacities at equilibrium conditions and at time t and $k_1(min^{-1})$ is the rate constant.

The pseudo-second-order kinetic model is expressed by the following equation

$$q_t = q_e^2.k_2.t/(1 + q_e.k_2.t)........... (6)$$

Where q_e (mg/g) and q_t (mg/g) are the maximum adsorption capacities at equilibrium conditions and at time t and k_2((g (mg. min)$^{-1}$) is the pseudo-second-order rate constant.

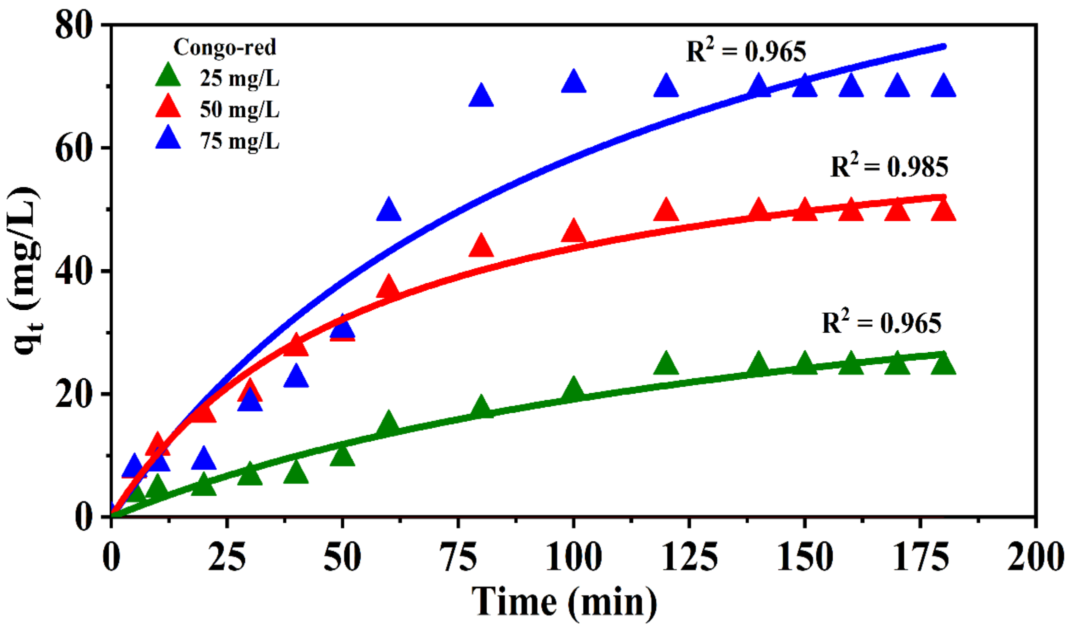

Figure 3.8: Pseudo-second-order model plot for Congo-red adsorption onto the CoAlFe-CO_3 (24 h) LDH, R^2 is correlation coefficient, model is applicable for high R^2 value (line indicates the fitting and dot indicates the q_t value).

Table 3.2: Pseudo-first-order and pseudo-second-order kinetic model parameters obtained in adsorption of Congo-red onto CoAlFe-CO_3 (24 h) layered double hydroxide.

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-second order			Pseudo-first order		
		$q_{2,cal}$ (mg/g)	$k_2(10^{-4})$ (g(mg. min)$^{-1}$)	R^2	$q_{1,cal}$ (mg/)	$k_1(10^{-5})$ (min^{-1})	R^2
25	50.616	24.494	1.203	0.965	5.265	-8.188	0.899
50	68.285	49.401	2.606	0.985	6.259	-8.227	0.933
75	124.741	70.501	7.065	0.927	7.746	-9.472	0.897

The conformity between the experimental data and model-predicted data was expressed by the correlation coefficient R^2. The analysis results are reported in Table 3.2. As can be seen from Table 3.2, with increasing the CR concentration from 25 to 75 mg/L, the pseudo-first-order constant k_1 decreases from -8.188×10^{-5} to -9.472×10^{-5} min^{-1} and pseudo-second-order constant k_2 increases from 1.203×10^{-4} to 7.065×10^{-4} $g.mg^{-1}.min^{-1}$. The correlation coefficient of the R^2 represents the suitable model for discussing the kinetic data. The R^2 of the pseudo-second-order model is greater than the pseudo-first-order kinetic model. So, this model is suitable to discuss the adsorption kinetics data. The pseudo-second-order model discusses the solid phase where adsorption occurred, consistent with the chemisorption mechanism. Another advantage of the pseudo-second-order kinetic model is that it predicts the whole reaction of the adsorption process [158].

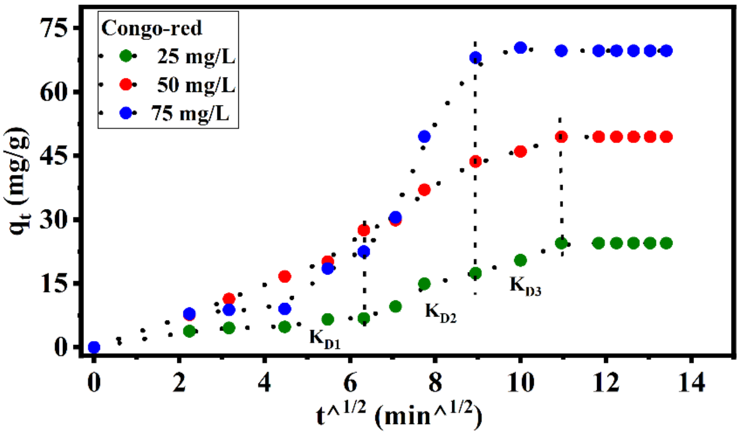

Figure 3.9: Intraparticle diffusion model for Congo-red adsorption onto the CoAlFe-CO_3 (24 h) LDH (T=25 °C, m=50 mg), dots represent the q_t value.

3.3.5.2. Intra-particle particle diffusion model

The intra-particle diffusion model (Figure 3.9) provides the possible mechanism as a function of time for Congo-red adsorption by the material. Diffusion, mass transfer, and adsorption onto the material's active sites were among the several complex steps in the adsorption process. In this case, there are three different stages for the adsorption process, which are attributed to external surface instantaneous adsorption (K_{D1}), gradual intraparticle diffusion (K_{D2}) and final equilibrium stages (K_{D3}), where the available active sites become saturated. The first step shows that higher adsorption occurred within 5 to 10 min. The second step is the rate-determining step due to intraparticle diffusion. The last step was also the rate-determining step; the equilibrium was reached due to the saturation of adsorption sites [163,164].

3.4. Adsorption capacity and isotherm model

In the solid-liquid system, the equilibrium of adsorption is one of the most important factors in investigating the maximum adsorption capacity of the material at different equilibrium adsorbate concentrations. The Langmuir and Freundlich isotherm models are two well-known models suitable for discussion in the work. These models yield a variety of factors that can be used to explain the adsorption mechanism, surface behaviour, and the affinity between the adsorbent and adsorbate. The models' correlation coefficient validated an appropriate fitted isotherm model. Table 3.3 illustrates that the Langmuir isotherm model is fitted for adsorption isotherm.

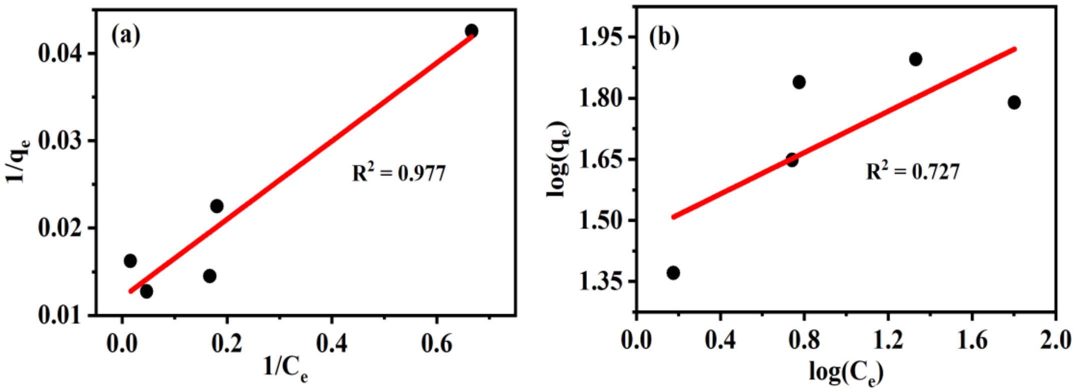

Figure 3.10: (a) The Langmuir (b) Freundlich isotherm model for Congo-red adsorption onto CoAlFe-CO_3 (24 h) LDH, the red line indicates the linear fitting and dot indicates the experimental value (R^2 of Langmuir isotherm is greater than Freundlich isotherm).

Table 3.3. Langmuir and Freundlich isotherm model constant and correlation coefficient for adsorption of Congo-red on the prepared sample at $T = 25 \pm 1\ °C$

Sample Name	Langmuir Isotherm	Freundlich Isotherm
CoAlFe-CO_3 (24 h) LDH	$q_m = 82.92$ mg/g $K_L = 0.269$ L/mg $R^2 = 0.977$	$K_f = 26.01$ mg/g $n = 3.61$

		$\frac{\mathbf{1}}{\mathbf{n}} = \mathbf{0.277}$ $\mathbf{R^2 = 0.727}$

According to the Langmuir isotherm model, a single monolayer of adsorbate resides in each active site on the adsorbent's surface, predicting that the energy used during the adsorption process will remain constant. The following equation describes the Langmuir isotherm model

$$\frac{1}{q_e} = \frac{1}{(q_m \times K_L \times C_e)} + \frac{1}{q_m} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The Langmuir isotherm model was utilised to compute the estimated maximum adsorption capacity q_m, which indicates full monolayer coverage on the adsorbent surface. The adsorption isotherm model of CR adsorbed by the materials is shown in Figure 3.10. The linear plot of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$, which gives the maximum adsorption capacity (q_m) as well as the Langmuir constant (shown in Table 3.3) [165]. The main reason for the adsorption process is the coulomb attraction force between the adsorbate and adsorbent because the surface charge of LDH is positive, while the dye charge is negative.

Table 3.3 illustrates the results of the linear plot of the Langmuir and Freundlich model. The correlation coefficient R^2 confirmed the suitable isotherm model to discuss the work. In this instance, the Langmuir isotherm model's R^2 is greater than the Freundlich model, suggesting a homogeneous adsorption process and the creation of a CR monolayer on the surface of the layered double hydroxide. The maximum adsorption capacity of CR by the CoAlFe-CO_3 (24 h) is 82.91 mg/g. The Freundlich isotherm model (Not Shown) predicted that the adsorption surface of the adsorbent becomes heterogeneous during the adsorption process. The Freundlich isotherm model constant K_f and n provides the approximate adsorption capacity and intensity of the adsorption process. The Freundlich isotherm model was described by the equation

$$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \; or \; q_e = K_f C_e^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

The curve plotted against log (q_e) vs log (C_e), which gives the value of K_f and n. where K_f, which stands for bonding energy, defines the adsorption or distribution coefficient and indicates the amount adsorbed by the adsorbent surface per equilibrium concentration [166,167]. The value of $\frac{1}{n}$ indicates the adsorption intensities of adsorbent or surface heterogeneity, which becomes more heterogeneity if the value of $\frac{1}{n}$ becomes close to zero. The value of $\frac{1}{n}$ less than 1 denotes a normal Langmuir isotherm process, whereas a value greater than 1 indicates a cooperative adsorption process [168]. Figure 3.11. All these results indicate that CR is adsorbed onto the LDH [169].

3.5. Possible adsorption mechanism

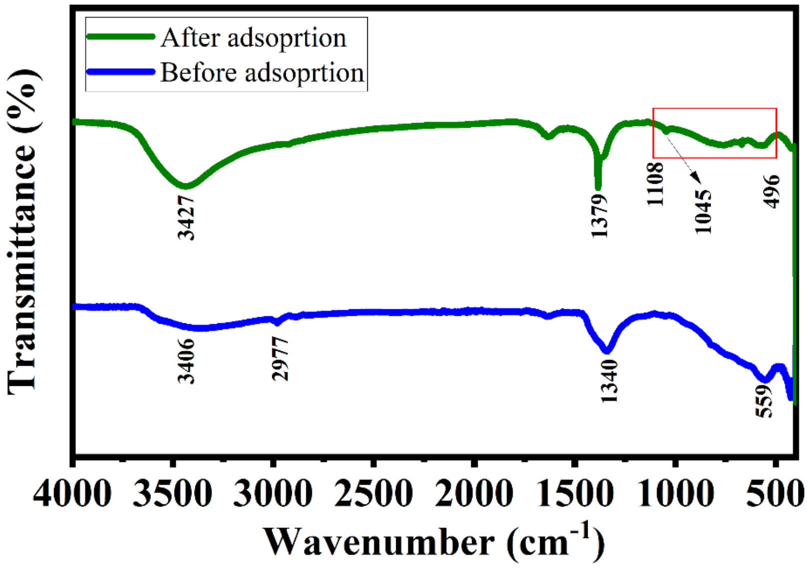

Figure 3.11: FTIR analysis of before and after adsorption onto the CoAlFe-CO_3 LDH.

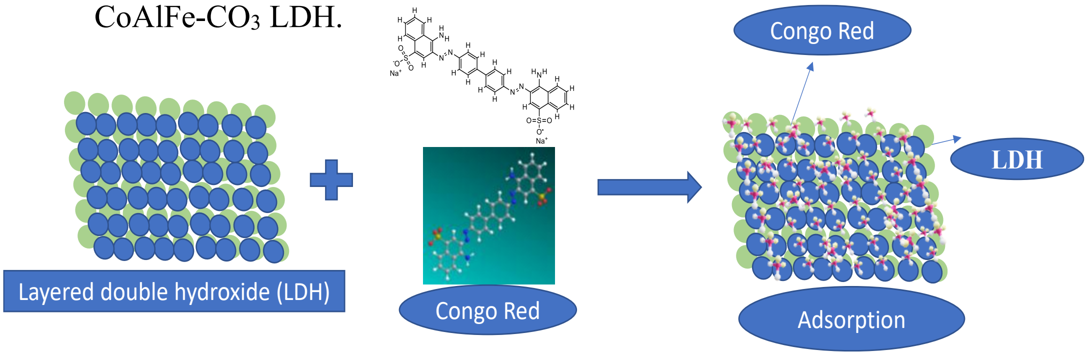

Figure 3.12: Schematic diagram of CR adsorption onto the CoAlFe-CO_3 (24h) LDH.

The adsorption mechanism is very important to understand the adsorption process. The characteristics of the adsorbent and adsorbate, such as their structure, functional groups, surface properties, and all types of interactions between the dye and LDH, are essential. The probable mechanism of CR onto the CoAlFe LDH was analyzed by the FTIR analysis and is shown in Figure 3.11. The broad peak associated with -OH at 3406 cm^{-1} shifted to 3427 cm^{-1}, suggesting a ligand exchange between CR and the hydroxyl group of CoAlFe LDH. The adsorption bands arising from the coupling between the benzene mode and the SO_3^- group are visible at 1045 cm^{-1}. In the range from 1108 to 496 cm^{-1}, additional peaks are visible.

The main mechanism behind the adsorption process is the force of attraction. The schematic diagram of the adsorption process is shown in Figure 3.12. The CR dye has a negative charge, and LDH has a positive charge, which is responsible for electrostatic interaction. Hydrogen bonding, electrostatic attraction, $n - \pi$ interaction and surface diffusion are all types of interactions that influence the adsorption process [170].

3.6. Conclusion

The CoAlFe-CO_3 LDH, ternary layered double hydroxide, was synthesised using the coprecipitation method at different synthesis times. The XRD spectra confirmed that the reaction time influences the structure of LDH. Significantly, the XRD analysis showed an increase in crystallinity as the reaction time increased, providing clear evidence of the impact of this parameter. The transmission electron microscopy images further revealed a uniform, well-defined, and lamellar structure of the layered double hydroxide structure, confirming the success of the optimization process.

The prepared material was successfully applied to remove CR from the aqueous solution. The pseudo-second-order model suitably fitted the kinetic data, while the Langmuir isotherm model fitted the isotherm data. The maximum adsorption capacity of CR by the CoAlFe-CO_3 (24 h) LDH, is 82.92 mg/g. This work suggests that prepared materials efficiently removed textile dye from the aqueous solution. Due to its positive surface charge, it is used as an adsorbent for congo-red adsorption. The best-fit isotherm data confirmed that the material is a promising adsorbent for removing anionic dye in the textile industry wastewater.