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Eco-friendly Approach for Effective Sorption of Congo Red Dye from Aqueous Solution Using NiAl LDH@DICD

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Abstract: Congo red dye, a prominent pollutant widely utilized in the textile industry, bestows significant challenges to environmental health and the aquatic ecosystems. In this study, we present a constructive approach through the development of a novel hybrid adsorbent, NiAl LDH@DICD, synthesized via simple co-precipitation method. This innovative material effectively combines pristine NiAl LDH with carbon dots derived from *Dillenia Indica*, leading to substantial improvements in dye removal efficiency while ensuring enhanced structural stability and reusability. Various characterization analyses provide confirmation of the successful synthesis and integration of carbon dots within the NiAl LDH matrix. High-Resolution Transmission Electron Microscopy (HRTEM) offers clear visual evidence of this incorporation, while photoluminescence (PL) study confirm the structural stability of the NiAl LDH@DICD. This robustness is vital for ensuring the adsorbent maintains its performance during repeated use. To assess the performance of NiAl LDH@DICD in removing Congo red dye from contaminated water, we carried out comprehensive batch equilibrium adsorption studies. The results highlighted that it follows the Freundlich isotherm model, indicating a heterogeneous multilayer adsorption process, achieving an R^2 value of 0.99. Notably, our adsorbent material achieved a dye removal efficiency of 87%, reflecting its considerable adsorption capacity even after three cycles of reuse. This research not only demonstrates the effectiveness of NiAl LDH@DICD as a reusable adsorbent for dye removal but also highlights its potential for sustainable applications in environmental remediation and also for heavy metal removal. The findings pave the way for further research aimed at advancing solutions for water treatment and pollution management, contributing to the development of more effective strategies for maintaining water quality.

Keywords: Layered Double Hydroxides; Adsorption, Dillenia Indica; Carbon Dots; Congo Red Dye

1. Introduction

Numerous industrial sectors such as textile manufacturing, dyeing plants, pulp and paper production facilities, as well as paint and ink manufacturers utilize immense volumes of dyes. Due to the stable nature and resistance to light, removal of dyes from wastewater poses a significant challenge [1]. Water pollution caused by synthetic dyes, such as Congo red, presents significant environmental challenges due to their toxicity and persistence. [1]. Consequently, there is a necessity to identify simple and cost effective methods for the elimination of dyes. Moreover, the presence of dye in water reduces the penetration of light, thereby causing depletion of photosynthetic activity in aquatic plants resulting in the origin of not only ecological issues but also aesthetic concerns [2,3]. Accounting to its toxic nature dyes have the capability to change the biochemical characteristics of fresh water system which leads to adverse effects on aquatic life.These bonds are formed with oxygen, nitrogen or sulphur atoms present in cellulose fibres, protein fibres and polyamides providing enhanced stability to fabric colour [4-6]. These presence of dyes with their potential to hamper human beings and aquatic environment must be controlled. Congo red dye, a type of synthetic dye characterised by its azo group is responsible for its vibrant colour. It is also known as anionic dye because it carries a negative charge [7,8].

Most of the organic dye, are responsible for bestowing color to food products and acquire aromatic centres within their molecular configuration. There are numerous methods which can be applied for the removal of dye pollutants including photocatalytic degradation, reverse osmosis, membrane filtration, flocculation, magnetic separation and electrodialysis [9-10]. But most of these methods generate secondary waste with high energy consumption, low removal capacity and highly expensive making them less sustainable for large scale applications. Hence these methods are not pertinent for the large scale treatment of dye contaminated water resources [11]. Adsorption on the other hand stands out as one of the common and effective wastewater treatment established on the principle of migration of solute molecules onto an active adsorbent surface [12, 13]. Due to these prevailing properties this technique has a great potential to be utilized at large scale industrial application.

Notably in the recent years, there has been an appeal in green chemistry due to its significance on cleanliness and sustainability [14, 15]. In this context, preparation of carbon dots using non-toxic solvents and economically viable green materials stands out as an essential aspect in green synthetic approach. Carbon dots are quasi-spherical materials formed mainly of carbon-based materials with typical sizes ranging from few to several tens of nanometers [16,17]. Being enveloped by functional groups like hydroxyl, carboxyl and amino groups on the surface they possess a graphitic core exhibiting excellent optical properties including strong fluorescence emission which can be tuned by controlling their size, synthesis conditions and surface functionalization. They are particularly valued for their low toxicity, biocompatibility and potential for green synthesis using renewable carbon sources [18-20]. Surface-passivated carbon dots are those which are characterized by the presence of oxygen containing functional groups on their surface namely –OH, -COOH and -C═O. Availability of multiple binding sites for interactions with various contaminants occurs as a result of these features which magnifies their surface reactivity [21-24]. Given this oxygen containing functional groups alongwith their features, carbondots are demonstrated to be an effective alternative material fortheremoval of wide rangeof pollutants. Different types of methods have been utilized for the synthesis of carbon dots including laser ablation, electrochemical techniques, hydrothermal methods, solvothermal process, microwave-assisted synthesis and ultrasonic irradiation. Among these hydrothermal methods stands out as the promising one [25-27].

Layered Double Hydroxides (LDH) which are also known as anionic clays are the type of materials comprising of detailed hierarchical structures encompassing divalent (M^{2+}) and trivalent (M^{3+}) cations accompanied by interlayer anion A^{2-} such as OH^-, CO_3^{2-} and Cl^-. The electroneutrality maintained within the structure is ensured by coulombic force of attraction between the intergallery anions and positively charged metals on the LDH layers [28,29]. These includes electrostatic attraction, ion exchange and Van der Waals force. Besides the interaction between the nitrogen or oxygen containing groups from adsorbates and hydroxyl groups of LDH results in the formation of hydrogen bonding. Nevertheless, in the adsorption process interactions of hydrogen bonding remains confined as the hydroxyl groups which remain unoccupied in the brucite-like sheets act as the binding sites for oxygen/nitrogen containing groups [30-32]. Furthermore, the cost-effective and reduced toxicity of LDH enhances its sustainability making it an environment friendly material [33,34].

Consequently, there exists a keen interest in fabricating tailored functional composite-based LDHs to augment the adsorption sites available for hydrogen bonding, thereby enhancing their overall adsorption capacity. Employing a strategy of fabricating composites through the assembly of positively charged layered double hydroxides (LDHs) and carbon dots possessing abundant oxygen-containing functional groups holds significant promise for contaminant removal. The adsorptive capacity of such composites was assessed using Congo red as a representative anionic dye. Although LDH surfaces inherently exhibit numerous hydroxyl groups, only the unoccupied hydroxyl groups within the LDH sheets are capable of forming hydrogen bonds [35-37]. In response to this pressing issue, this study develops an innovative eco-friendly material, NiAl LDH@DICD, which is designed for efficient dye adsorption. By combining the adsorption capabilities of layered double hydroxides (LDHs) with functionalized carbon dots, this approach not only enhances dye removal efficiency but also contributes to the advancement of sustainable solutions. By bridging these gaps, the study demonstrates the promising efficiency of the NiAl LDH@DICD material in dye removal. The results highlight its potential for sustainable wastewater treatment, offering valuable insights that can further the development of eco-friendly sorption technologies. Accordingly our synthesized adsorbent was prepared and employed to examine the removal of Congo Red dye from aqueous solutions. It was further observed that the adsorbent exhibited significant removal efficiency of dye molecules. The adsorbent was thoroughly characterized using techniques such as PXRD, SEM & EDX, FTIR, HRTEM, BET Surface Area, TGA, PL. Additionally the adsorption parameters were systematically studied.

2. Materials and Methods

2.1. Materials

Dillenia Indica was collected from the local place Kokrajhar, Assam, India. Nickel Chloride hexahydrate ($NiCl_2.6H_2O$), Aluminium chloride ($AlCl_3$), NaOH, $NaHCO_3$ and Congo Red dye were used. All the chemicals used in this experiment were obtained from Merck and were of analytical grade. The required solutions were prepared by deionised water.

2.2. Preparation of Ni-Al LDH

NiAl LDH was prepared via co-precipitation method. 2M of Nickel Chloride hexahydrate ($NiCl_2.6H_2O$) solution and 1M of Aluminium Chloride ($AlCl_3$) solution was taken and mixed in a beaker. Simultaneously, 1M of $NaHCO_3$ was added in the resultant metal precursor solution in which 2M of NaOH solution was added in order to maintain pH of 11. The resultant solution was left undisturbed and left for decantation for 24 hours. It was then centrifuged at 1500 rpm and then re-dispersed in distilled water and then centrifuged again. This was done in order to remove any impurities left. And it was then dried in hot air oven at 70ºC and then collected. The resultant blue coloured powdered substance is the NiAl LDH.

2.3. Preparation of CD using Dillenia Indica

The synthesis of carbon dots using *Dillenia Indica(DI)* fruit shells were conducted by the pyrolysis method. This method includes collecting the *Dillenia Indica* fruitscommonly known as *Ou Tenga.* The fruit shells were meticulously cleansed with distilled water to eliminate any potential impurities. Subsequently, the fruit shells were dried completely under sunshine and in an oven to completely remove moisture. The shells were then broken into small pieces and then grinded into fine powder to ensure uniform heating. Following this, the powdered material is then subjected to thermal decomposition, which is known as pyrolysis by heating it in a muffle furnace for 200ºC for 2 hours. This carbonized material was then dissolved in water and is then sonicated to breakdown larger particles. The resulting solution is then filtered to remove further impurities which were then subjected to centrifugation procedure which was repeated 2-3 times to eliminate any fine suspended particles. The filtrate was further purified with a filtration membrane and stored at 15°Cfor subsequent applications. This was done in order to prevent their photoluminescent properties and prevent the degradation of surface functional groups.

2.4. Fabrication of LDH-Carbon Dot Solution

The LDH-carbon dot solution was synthesized employing the colloidal deposition method. Initially, 3gm of Ni-Al LDH were meticulously combined with 6ml of the carbon dot solution and subjected to vigorous stirring at ambient temperature utilizing a magnetic stirrer. Subsequent to the stirring process, the mixture was then permitted to settle undisturbed for approximately 60 minutes, facilitating thorough interaction. Following this incubation period, the resultant mixture underwent final drying in an oven set at 60ºC, culminating in the removal of residual moisture, and was subsequently stored for subsequent applications.

2.5. Characterization

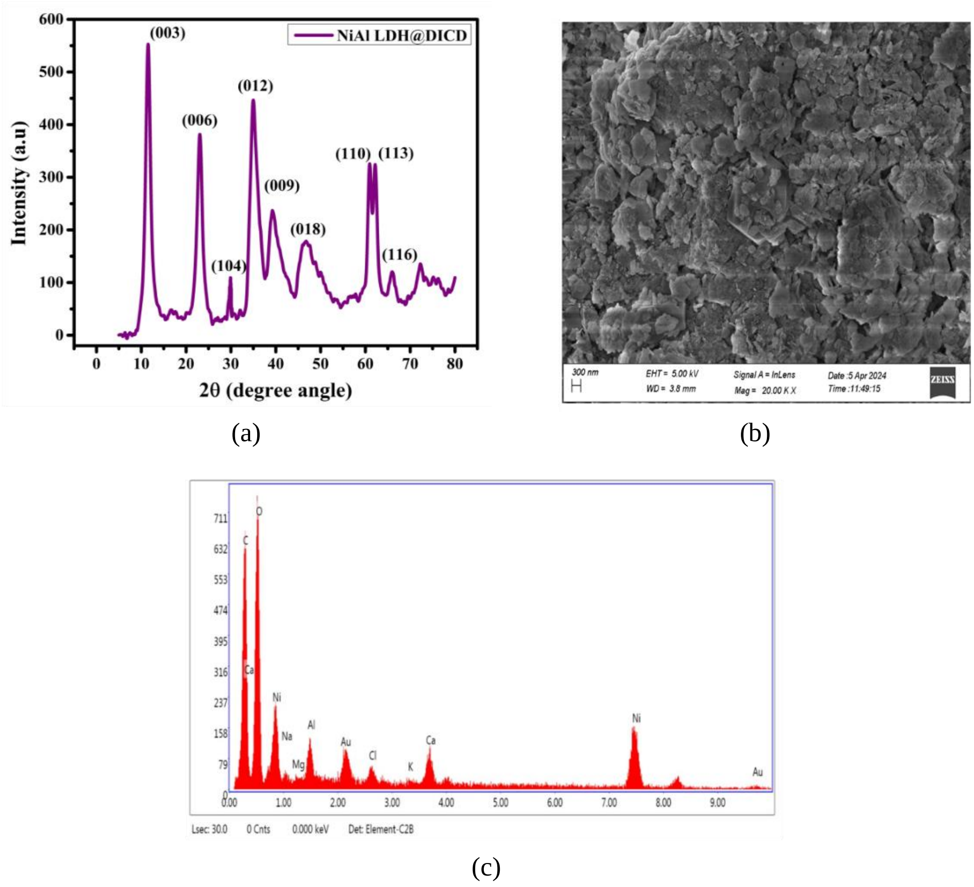
Several characterization techniques were used to characterize the synthesized adsorbents. Firstly we recorded the PXRD diffractogram with a Rigaku Ultima IV X-Ray Powder diffractometer, using Cuα $\lambda = 1.54$ Å as X-Ray source. The data was collected in the 2θ range from 0 to 80 degrees. To observe the shape and structure we used Zeiss SEM and further examined the composition of elements using EDX. The specific surface area and pore size was calculated by conducting nitrogen adsorption-desorption test with BET surface area and BJH method using Quantachroma, Autosorb-IQ MP. The FTIR spectra were taken with Bruker IR-Alpha, using KBr as reference within the frequency range from 400-4000cm^{-1}. we also assessed the thermal stability of the adsorbent through Thermogravimetric Analysis (TGA) with a Mettler Toledo Instrument. For measuring heavy metal concentrations, we used UV-spectrophotometer-3375 from electronics India. Lastly we examined the internal structure of the adsorbent using HRTEM from JOEL at an accelerating voltage of 200kV.

Photoluminescence (PL) was analysed using Photoluminescence spectrometer (Cary Eclipse Agilent).

2.6. Adsorption Experiment

The adsorption potency of the prepared adsorbent was investigated at room temperature using a batch equilibrium method. For isotherm studies, solutions of Congo Red dye having initial concentration of 20 mg/L and ranging upto 160 mg/L was prepared in conical flask, with each containing 30 ml of the solution. This was followed by the addition of 0.025 gm of the prepared adsorbent into each of the dye solutions which were then transferred into thermostatic shaker. The mixtures were then agitated for upto 3 hours in order to achieve equilibrium adsorption. After the completion of stirring period, the adsorbent material was separated from the resultant dye solution by filtration. The clear solution was later analyzed using UV-vis spectrophotometer for determining the concentration of Congo Red dye.

3. Results and Discussion



(a) (b)

(c)

Figure 1. (**a**) PXRD spectra of NiAl LDH@DICD; **(b)** SEM images of NiAl LDH@DICD; **(c)** EDX spectra of NiAl LDH@DICD

The Powdered X-Ray Diffraction (PXRD) of the prepared adsorbent (NiAl LDH@DICD) was analyzed to assess the crystalline structure and to identify the crystallographic plane within the material as illustrated in Figure 1 (a). The peak observed at

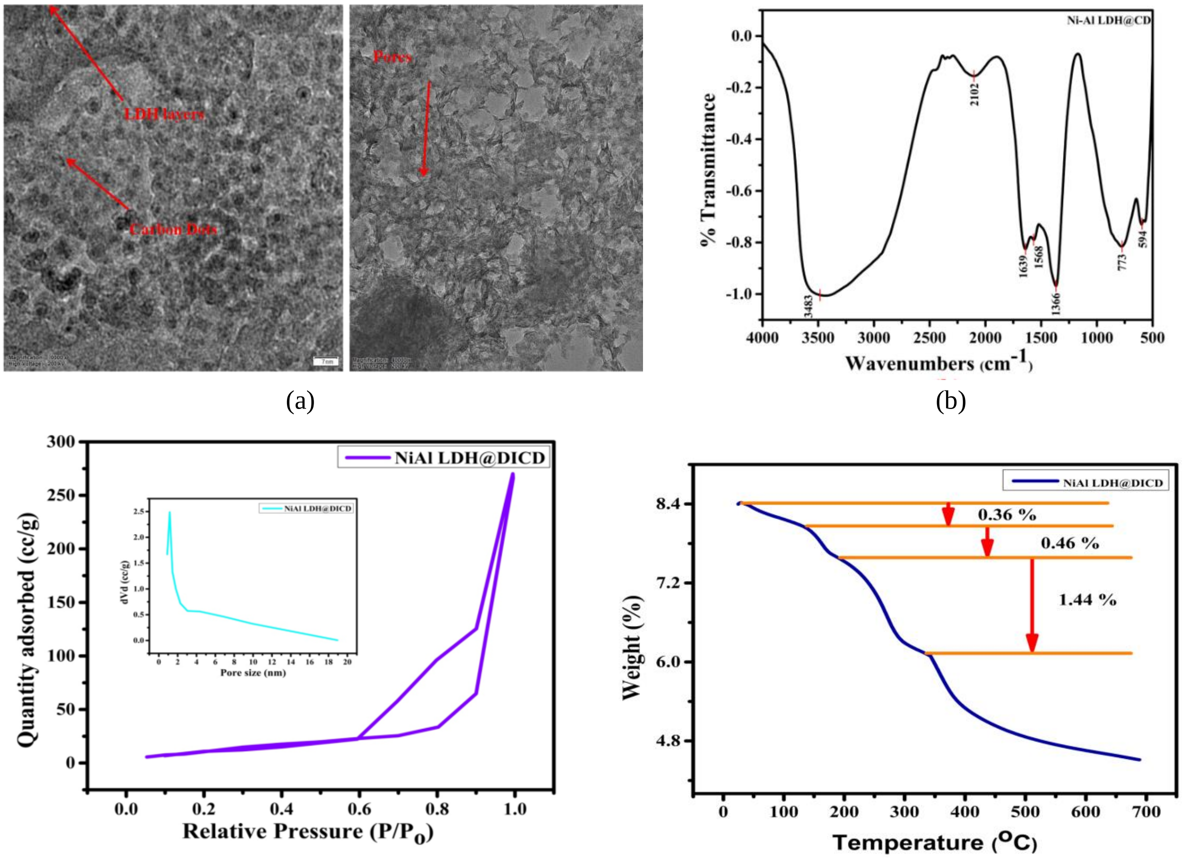
(003) indicates the basal reflection pattern, corresponding to the interlayer spacing thereby confirming the presence of layered structure within the NiAl LDH@DICD. The peaks at (006) and (009) planes further suggest the periodicity of the layers thereby confirming its crystalline nature [38]. The new short intense peak at (104) further highlights the possible intercalation of green carbon dots. The presence of peaks at (012), (110) and (113) supports the well-defined crystalline nature of the material and that it has not been disrupted even after its modification. Nevertheless the peaks occurring at (018) and (116) highlights the ordered nature of the layers [39].

The SEM analysis of NiAl LDH@CD is represented in Figure 1 (b). As it can be clearly observed from the above figure there is formation of intriguing flower like structures, which confirms the presence of carbon dots within the NiAl LDH@DICD structure. Introduction of the green carbon dots causes some structural transformations, which implies to act as nucleation centre leading to the growth of curved LDH layers into intricate patterns. These green carbon dots having unique functional groups tend to tailor the interactions between the LDH layers resulting in increased surface area provided by the flower like structures. This increment further improves the material's functionality in various adsorptions, catalytic processes. The accumulation of this flower like patterns indicates that the green carbon dots play a decisive role in altering the layered structure of NiAl LDH. The EDX analysis of NiAl LDH@CD is illustrated in Figure 1 (c) which reveals the presence of various key elements. The elemental composition of the prepared NiAl LDH@CD is C (25.10%), O (25.84%), Na (0.21%), Al (2.34%), Cl (1.01%), Ni (37.27%) and Mg (0.05%) respectively.

The High- Resolution Transmission Electron Microscopy (HRTEM) analysis of NiAl LDH@DICD provides a detailed insight into the material's microstructure including the distribution of carbon dots as well as the porous structure as elucidated in Figure 2 (a). The HRTEM images of the prepared adsorbent revealed existence of carbon dots which are uniformly distributed across the NiAl LDH@DICD structure at an observable range of 7 nm proving the successful intercalation of the carbon dot solution into the LDH structure. Further analysis at 100 nm range revealed the presence of well-defined pores within the structure recommending a mesoporous structure which facilitates the enhanced ion transportation within the structure. This porous framework not only holds the orderly distribution of CDs but also provides a significant surface area for interaction. Furthermore, amalgamation of these nanoscale features tailors the materials functional properties, making it a promising adsorbent in adsorption benefiting from its high surface area and pore size.

The FTIR spectra of NiAl LDH@CD are depicted in Figure 3 (b). The broad peak at wavenumber 3483 cm^{-1} corresponds to the interaction of the hydrogen bonding between NiAl LDH and *Dillenia Indica* carbon dots. The band at 2101 cm^{-1} is related with the presence of $C\equiv N$ stretching vibrations, which is indicative of nitrile or similar functional groups introduced through carbon dots modification. Another peak at 1639 cm^{-1} depicts H—O—H bending vibrations, which are related to water molecules that are being adsorbed and commonly seen in LDH materials highlighting the adsorbent's ability to retain moisture. The peak occurring at 1568 cm^{-1} is a characteristic of stretching vibrations of $C=C$ bond. Also the band occurring at 1366 cm^{-1} represents the asymmetric stretching of carbonate ions

(CO_3^{2-}). Nevertheless the observed peaks at 733 cm^{-1} and 594 cm^{-1} were attributed to M—O—M (metal-oxygen-metal) lattice vibrations.



(a) (b)

(c) (d)

Figure 2. (a) HRTEM images of NiAl LDH@DICD; **(b)** FTIR spectra of NiAl LDH@DICD; **(c)** BET Surface Area of NiAl LDH@DICD; **(d)** TGA of NiAl LDH@DICD

The Brunauer-Emmett-Teller (BET) surface area analysis of the adsorbent NiAl LDH@DICD is illustrated in Figure 2 (c). The analysis revealed a type IV adsorption isotherm curve common for mesoporous materials. This type of isotherm is being associated with monolayer-multilayer adsorption adsorption at relatively low pressure, which is followed by a hysteresis loop at high pressure. The specific BET Surface Area was determined to be 127.74 m^2/g while the pore diameter and pore volume was measured to be 1.21 nm and 0.071 cm^3/g which falls well within the mesoporous range. The indication of high surface area recommends large, accessible surface which is benign for adsorption applications.

Thermogravimetric Analysis (TGA) of NiAl LDH@DICD was done in order to assess its thermal stability as illustrated in Figure 2 (d). The analysis depicted a potential first mass loss at 0.36 %, which is observed at lower temperatures. This minor reduction in weight loss occurs as a result of discharge of physically adsorbed water on the LDH surface. The second reduction in mass with a value 0.46 % occurring within temperature range of 150-300ºC is related to decomposition of interlayer hydroxyl groups which further elucidates the removal of more strongly constrained water molecules within the LDH layers. The third and final loss of mass at 1.44 % took place at higher temperatures ranges of around 300-500ºC. This significant weight loss is in correspondence with the decomposition of the organic groups from *Dillenia Indica* carbon dot solution incorporated with NiAl LDH.

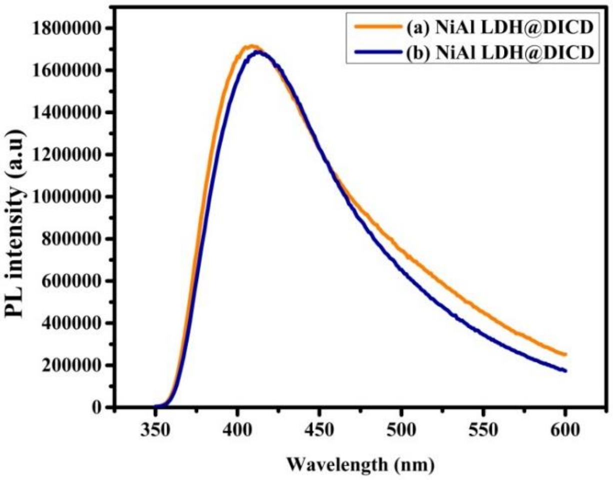
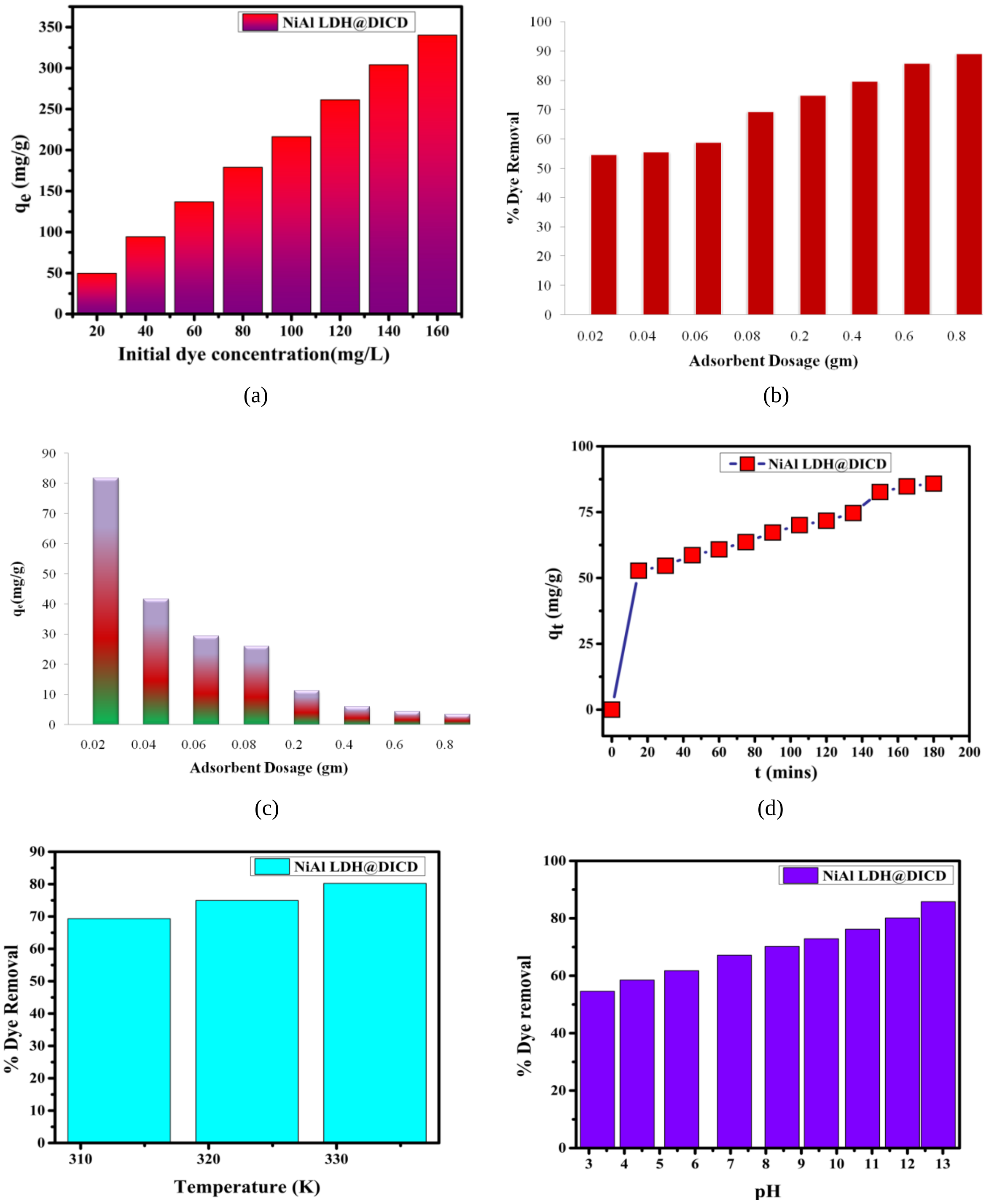


Figure 3. Photoluminescence analysis of NiAl LDH@DICD

Photoluminescence (PL) of NiAl LDH@DICD was analysed which gives a characteristic behaviour of the prepared adsorbent mixed with green carbon dots as indicated in Figure 3. The prepared material was excited at different wavelength of 330 nm and 340 nm [Figure 3 (a) and (b)]. The PL emission was recorded at 408 and 413 nm. The adsorbent material when excited at 330 nm showed an emission wavelength at 408 nm which implies radiative recombination associated with electronic transitions within the LDH matrix which is enhanced by green carbon dots. This introduces new surface states thereby boosting emission intensity. The material was further excited with wavelength at 340 nm produced an emission at 413 nm displaying a slight red shift compared to the emission at 330 nm. This proves that with the decrease in excitation energy, the emission process is influenced by additional defect states or surface energy levels introduced by carbon dots. The capability of green carbon dots to succumb to similar emission wavelengths at different excitation wavelength indicates its capability of high level with the NiAl LDH matrix.

3.1. Effect of Adsorption Parameters

Congo Red dye solution was investigated at different initial concentrations (20-160 mg/L) with having adsorbent dosage at 0.25 gm and 180 minutes of contact time at room temperature which is plotted and presented in Figure 4 (a). In the following study it was found that the adsorption capacity q_e goes on increasing with the increment in concentration of initial dye (49.65 to 340.22 mg/L). With the increase in concentration of dye NiAl LDH@DICD displays higher adsorption capacity suggesting that the prepared adsorbent possesses a considerable capacity to accommodate high load of dyes. This results due to the π—π interaction and electrostatic forces acting between the dye molecules and NiAl LDH@DICD surface. Existence of this dual interaction property of carbon dots enhances these interactions by contributing more active sites. These carbon dots are likely contributing additional functional groups like various hydroxyl and carboxyl groups which engages in interactions like hydrogen bonding and electrostatic synergy with the dye molecules.



(a) (b)

(c) (d)

(e) (f)

Figure 4. Effect of **(a)** initial dye concentration; **(b)** & **(c)** adsorbent dosages; **(d)** time study; **(e)** temperature study; **(f)** pH of NiAl LDH@DICD

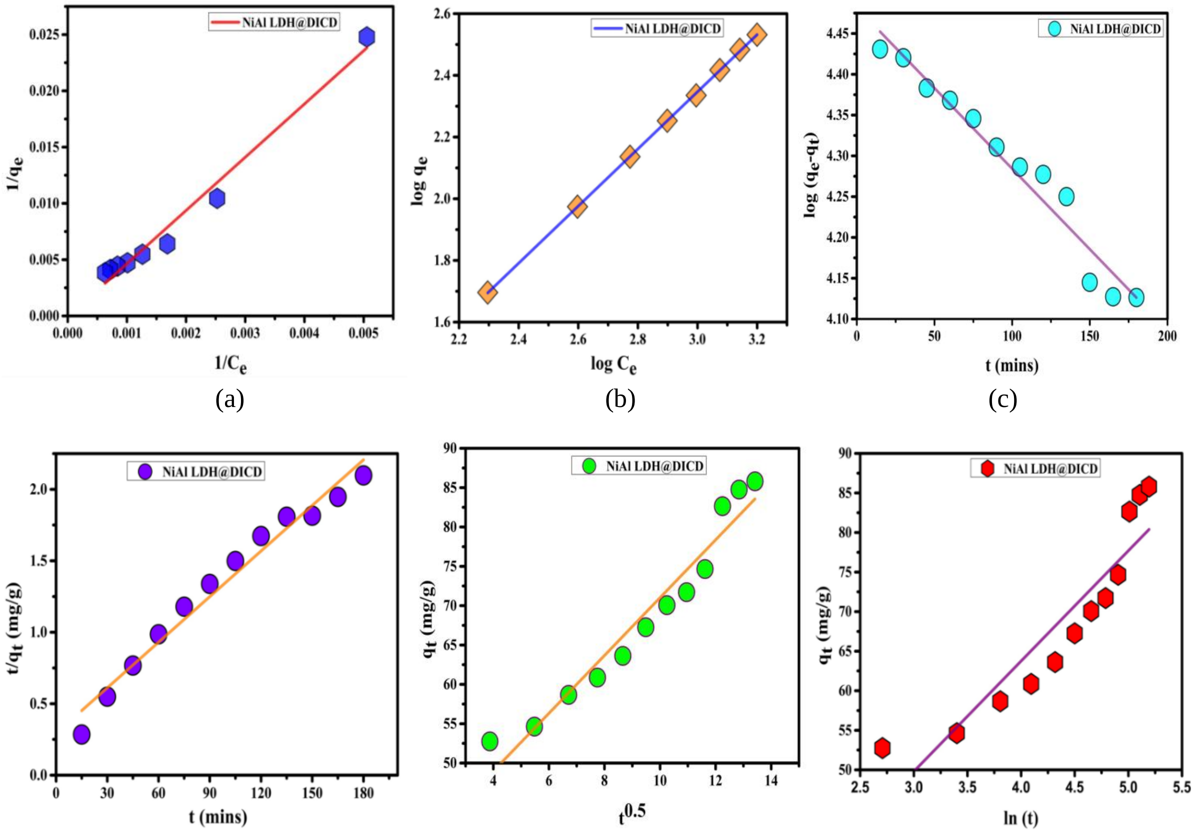
The effect of the quantity of the adsorbent during adsorption process plays a vital role in significance of its adaptability. To investigate the impact of dosage for CR reduction, the adsorbent quantity was altered from 0.02 to 0.8 gm as indicated in Figure 4 (b,c). From the figure it can be clearly seen that rise in adsorbent dosages from 0.02 gm to 0.8 gm lead to a progressive increase in dye removal percentage achieving an efficiency of 87 %. This reflects the phenomenon that at higher adsorbent dosages, there is availability for more active sites for interaction with the dye molecules, expediting greater dye removal from the solution. Meanwhile with the increased adsorbent dosage, adsorption capacity (q_e) exhibited a decreasing trend attributing to the redistribution of dye molecules across the larger number of available adsorption sites.

The influence of contact time regarding adsorption capacity of the prepared adsorbent was studied under initial dye concentration having 60 mg/L and adsorbent dosage of 0.025 gm. Figure 4 (d) demonstrates the effect of contact time on the adsorption of Congo red dye onto NiAl LDH@DICD. The time-dependent study showed that the adsorption capacity (q_t) increased at rapid rate within the first 15 minutes reaching a value of 52.75 mg/g, indicating the availability of large number of active sites on the adsorbent surface allowing for the fast interactions and binding of molecules of dyes. Also as the adsorption experiment further progresses the concentration gradient between the dye solution and the adsorbent surface diminishes causing a reduction in the driving force of the adsorption. Nevertheless between 165 and 180 minutes the adsorption process shows minimal increment referring that the adsorption process is nearing equilibrium and that all the active sites have been occupied.

The outcome of temperature effect for the removal of Congo Red dye using NiAl LDH@DICD is illustrated in Figure 4 (e). Upon examining the influence of temperature it was observed that the removal percentage of dye escalated successively alongwith the rise in temperature. The enthalpy change ΔH for Congo Red dye adsorption over NiAl LDH@DICD was calculated and the value was found to be 26.93 KJ/mol. This positive value for enthalpy change depicts that the process is endothermic and that rise in temperature (310K to 330K) amplifies the kinetic energy of dye molecules, resulting in more frequent and effective collisions with adsorbent surface.

The pH value of an aqueous solution is an important factor which affects the removal of Congo red dye. The reduction in Congo red dye was evaluated over a pH spectrum range of 3-12 at C_0 = 60 mg/L Figure 4 (f). Binding state of the adsorbent as well as the ionization degree can be varied with subsequent change in pH of the solution. The study revealed that at low pH values the surface of NiAl LDH@DICD becomes protonated causing a reduction in its compatibility with dye molecules. However as the pH shifts to alkaline medium surface of NiAl LDH@DICD become negatively charged as a result of deprotonation of surface hydroxyl groups. The maximum removal efficiency of Congo red dye was observed at higher pH values affirming about the favourability of adsorption in alkaline medium.

The experimental isotherm was analyzed based on Langmuir, Freundlich isotherm models which is illustrated in Figure 5 (a, b). From the experimental findings the adsorption isotherm has Freundlich adsorption isotherm model with R^2 value of 0.99 much closer to unity as compared to Langmuir isotherm model having R^2 value of 0.97. So the adsorption isotherm follows Freundlich isotherm model and it's suitability into this model assumes that the adsorbent has multilayer adsorption, accommodating with interactions of Congo Red dye molecules on surface of NiAl LDH@DICD. The heterogeneous surface of the prepared adsorbent composed of Layered Double Hydroxides and *Dillenia Indica* carbon dot solution enhances the rate of adsorption. This further proves its co-relation with Freundlich adsorption isotherm model which allows for adsorption within multiple layers and does not endorse uniform adsorption energy across the surface.



(a) (b) (c)

(d) (e) (f)

Figure 5. (a) Adsorption isotherm Langmuir; **(b)** Freundlich; **(c)** Pseudo first order kinetics; **(d)** Pseudo second order kinetics; **(e)** Intraparticle dffusion model; **(f)** Elovich model of NiAl LDH@DICD

For the kinetics study the experimental findings were analyzed by Pseudo first-order (PFO), Pseudo second-order (PSO), Intraparticle diffusion and Elovich model which are depicted below in Figure 5 (c, d). The R^2 value corresponding to Pseudo second-order is much closer to unity as compared to Pseudo first-order which concludes that it follows PSO kinetics. Fitting of the data into this model suggests that chemical adsorption or chemisorption is the underlying mechanism which is being involved in the kinetic studies including interactions like covalent bonding, electron sharing or ion exchange.Chemisorption implicates activation energy which is higher than physisorption and is characterized by enhanced interactions between the adsorbate and the adsorbent leading to formation of multilayer. The adsorption data was further analyzed with Intraparticle diffusion model and Elovich model, where the material was found to fit with Intraparticle diffusion model as compared to Elovich model as illustrated in Figure 5 (e, f). The intraparticle diffusion model allows the adsorption process to occur in multiple stages. Initially it occurs through the surface adsorption followed by gradual diffusion into the interior of the adsorbent. Congo red dye substantiates a fast adsorption process on NiAl LDH@DICD likely due to the binding at surface which is followed by slower phase where dye molecules diffuse into adsorbent's interlayer spacing. This type of behaviour is acquired effectively by the intraparticle diffusion model, where the boundary layer effects administer insight into the initial resistance.

The effect of reusability of adsorbents is crucial for their efficient utilization in various application. The reusability performance of NiAl LDH@DICD was executed upto third cycles under a constant experimental condition having initial concentration of 60 mg/L, with 0.025 gm of adsorbent quantity and agitating it for 3 hours, Figure 6. After each consecutive cycle, the adsorbent was washed comprehensively with ethanol as well as deionised water which was further observed for reusability test. The first removal cycle illustrates high removal efficiency, 82% due to the presence of numerous active sites including functional groups due to carbon dots. However in case of second reusability cycle, the removal percentage decreases significantly to 78%. This occurs as a result of the sites which are being partially occupied by the dye molecules. Nevertheless in the third cycle, removal efficiency was further reduced to 72 % which arises due to rapid adsorption-desorption.

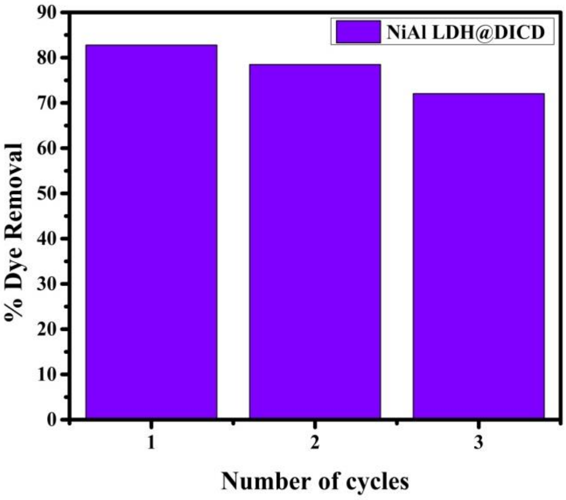


Figure 6. Reusability studies of NiAl LDH@DICD

Table 1. Catalog of adsorption efficacy of NiAl LDH@DICD with other NiAl LDH based adsorbents

Adsorbent	Method of preparation	Targeted Dye	BET Surface Area (m^2/g)	Contact time (min)	Adsorption capacity (mg/g)	Regeneration cycle	Reference
Ni/Al-CLDH-H	Co-precipitation	Congo Red	153.3	180	1229.59	6	[40]
NiAl LDH/BC		Malachite Green	220.9	150	142.8	3	[41]
Ni/Al-GF		Congo Red	438.942	200	116.29	5	[42]
Ni/Al-BC		Congo Red	21.595	200	312.5	5	[42]
NiAl LDH@DICD		Congo Red	127.74	180	237.84	3	This work

In the present study a novel adsorbent material NiAl LDH@DICD was synthesized through simple straightforward preparation method, resulting into a material with notable adsorption property. Particularly at alkaline conditions the adsorbent material displayed high removal efficiency. Characterization revealed a noteworthy BET Surface Area of 127.74 m^2/g and from additional analysis it was also found that it follows Freundlich adsorption isotherm model. Alongwith this, the prepared adsorbent has an excellent removal efficiency of 87 %. Nevertheless, the present work as also compared with those of other works is illustrated in Table 1. From the table it has been found that while most of the previous studies showcases the high removal efficiency of dyes by NiAl LDH precursor but some of them involve the use of chemical agents. Although some of the studies have explored the use of biochars however their removal efficiency was lower coupled with longer equilibrium time taken. In contrast our work showcased significant improvement in removal efficiency within a stipulated equilibrium time of 180 minutes. This was achieved through a simple and sustainable green synthesis method utilizing carbon dot solution derived from *Dillenia indica*.

4. Conclusions

To conclude, the pristine NiAl LDH was prepared successfully by co-precipitation method and *Dillenia Indica* based carbon dots were incorporated successfully onto NiAl LDH. This study demonstrates the effectiveness of the prepared adsorbent for the removal of Congo red dye achieving a removal efficiency of 87%. HRTEM analysis confirmed the successful incorporation of the carbon dots onto the pristine LDH structure as well as the porous nature of it while SEM analysis highlighted the well-defined hexagonal layered structure. Further validation by BET surface area analysis displayed high surface area thereby proving that the prepared adsorbent plays a key role in adsorption application. Furthermore the adsorption process fits well in Freundlich isotherm model, aligning itself with the heterogeneous surface characteristics of NiAl LDH@DICD, signifying that the adsorption occurs on surface having varied sites. Reusability studies proved that the adsorbent maintains a good performance for up to 3 cycles. Although with each increasing cycle there is decrease in efficiency indicating its potential for multiple uses in practical applications. Further research will focus, regarding the adaptation of the prepared material for the treatment of various pollutants and exploring its potential catalytic applications which willcontinue to develop sustainable solutions to address environmental pollution effectively.

Multidisciplinary Domains

The research covers the following domains: (a) Water Management, and (b) Environmental Science.

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Conflicts of Interest

The authors declare no conflict of interest.

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