Kinetics and isotherm studies for the adsorptive removal of Reactive Red-141 dye from aqueous solution by uncalcined and calcined zinc aluminium carbonate layered double hydroxide- A comparative study

K Manjula Rani* & P N Palanisamy

Centre for Environmental Research, Department of Chemistry, Kongu Engineering College,
Perundurai, Erode 638 060, Tamilnadu, India

E-mail: chemistrykmr@gmail.com

The feasibility of the removal of Reactive Red -141 (RR-141) by two different adsorbent materials namely zinc aluminium carbonate layered double hydroxide (ZAC-LDH) and calcined LDH (CZA-LDH) from aqueous solution has been investigated. To investigate the adsorption capacities of the adsorbent, batch mode adsorption studies has been performed for the removal of RR-141 using different parameters such as initial dye concentration, adsorbent dosage, contact time, temperature and pH. The various adsorption kinetic studies such as pseudo first order, pseudo second order and intra particle diffusion models are performed. The pseudo-second-order kinetic model is fitted well with high correlation coefficient. The optimum pH for maximum dye removal is found to be highly acidic (i.e., pH 2). Both Langmuir and Freundlich isotherm models described the adsorption mechanism of dye by both the adsorbents. The FESEM images and XRD pattern confirmed that the adsorption and intercalation of RR-141 dye molecule onto the adsorbents. The thermodynamic parameters like ΔG°, ΔH° and ΔS° have also been calculated. Regeneration of calcined and its reusability has also been performed for the removal of RR-141. The results suggest that the efficiency of CZA-LDH is found to be good enough to remove RR-141 comparatively with the uncalcined LDH sample ZAC-LDH from aqueous solution.

Keywords: Batch adsorption, Calcined layered double hydroxide, Isotherm, Kinetics, Reactive Red-141, Thermodynamics

Environmental pollution due to discharge of industrial effluents from textile, tanneries, cosmetics, paper, pharmaceutical, printing and other industries became a serious one because of its visibility, toxicity[1] and non-biodegradability[2]. Even a trace quantity of dye release into an aquatic ecosystem is hazardous for the aquatic life in terms of hindering photosynthetic activity[3]. Many of the dyes used in our daily life may undergo degradation to form highly toxic and carcinogenic products[4]. The removal of color from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. Traditional technologies such as biological[5] coagulation and electrochemical techniques[6,7], advanced oxidation process as well as membrane processes[8] are generally ineffective for total colour removal. Because of high capital and operating cost required for traditional and conventional methods, it is necessary to develop low cost methods and materials to clean up contaminants in the environment.

Several methods have been developed like adsorption, photocatalysis[9], Ozonation[10], chemical oxidation[11], microbiological or enzymatic decomposition[12] for the removal of colour from wastewater. The removal of synthetic dyes from wastewaters is especially difficult when reactive dyes are present, for which conventional wastewater treatment plants give low removal efficiency[13]. Reactive dyes are mainly used to dye cellulosic fibres like cotton. During dying of reactive dyes on cotton, covalent bond is formed between the dye and the fibre with loss of considerable amount of dye in the effluent leads water pollution.

Adsorption process is regarded as one of the effective process for the removal of dyes and heavy metals because of its high efficiency, simplicity of design and cost effective operation[14]. Activated carbon is a widely used and effective adsorbent, but its use is limited by the high costs associated with its regeneration. Many researchers have employed various adsorbents prepared from waste materials

such as orange peel, banana peel, lemon peel, raw barley straw, egg shell, sawdust, rice husk, coir pith carbon and tea waste.

Among different adsorbents, layered double hydroxides (LDHs) are cheap and nontoxic materials belonging to the class of anionic clays[15] which is employed as waste scavengers, particularly for dye molecules[16]. The general formula of LDHs is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} is divalent metal (Zn^{2+}, Mg^{2+}, Fe^{2+} etc), M^{3+} is trivalent metal (Al^{3+}, Fe^{3+} etc), and A^{n-} is interlayer anions (CO_3^{2-}, Cl^-, NO_3^-, SO_4^{2-} etc.,)[17,18]. Carbonates are the interlayer anion present in naturally occurring mineral hydroxide which is a member of this class of materials. LDH material showed a large flexibility of composition that can be made by using the different nature of the divalent and trivalent cations in the layers, the type of interlayer anions (A^{n-}) and the stoichiometric coefficient (x)[19]. These materials find wide applications in various fields, such as catalysis, adsorbents, ion exchanges, pharmaceutics, purification, etc.[20-24] due to its flexibility in composition and the exchangeability of interlayer anions. Calcination of LDHs around 550°C destroys the layered structure of the clay and gives rise to porous mixtures of mixed oxides. Using "structural memory effect", the layered structure of these clays can be reconstructed when the mixed oxides (calcined LDH's) are exposed to aqueous solutions of anions. The anions used during the reconstruction process need not be the same and may be different from those of the original LDH's [25].

The aim of the present study is to synthesize Zinc aluminium carbonate layered double hydroxide (ZAC-LDH) and calcined Zinc aluminium Layered Double Hydroxide (CZA-LDH) and also employed as adsorbent for the removal of Reactive Red-141 from aqueous solution.

Experimental Section

Preparation of zinc aluminium carbonate Layered Double Hydroxide (ZAC-LDH) and CZA-LDH

Zinc Aluminium carbonate layered double hydroxide (ZAC-LDH) was synthesized using aqueous solution of $ZnSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 16H_2O$. The aqueous solution of Zinc sulphate (1M) and Aluminium sulphate (1M) were taken in the molar ratio $M^{2+}/M^{3+}=3$ and mixed in magnetic stirrer. Exactly 0.3 g of CTAB was added to the solution and made the solution as a homogeneous mixture with a magnetic

stirrer. Precipitating agent sodium hydroxide (1M) and intercalating carbonate anion source sodium carbonate (0.5 M) mixture was added drop wise until the pH was 9. The precipitate was poured into Teflon lined stainless steel autoclave and heated to about 120°C and maintained for about 8 h. The synthesized material was filtered, washed several times with double distilled water until the pH was neutral and dried at 80°C in hot air oven. The obtained product was named as ZAC-LDH. The calcined ZA-LDH was obtained by heating the original ZAC-LDH in a muffle furnace at 450°C for 2 h in an air atmosphere with heating and cooling rates of 10°C/min. Both ZAC-LDH and CZA-LDH samples were finely grinded and used for the analysis and adsorption studies.

Characterization

X-ray diffraction (XRD) pattern of the sample was characterized by using a Shimadzu XRD-6000 diffractometer, with Ni-filtered Cu-Kα radiation (λ= 1.54 Å) at 40 kV and 200 mA. Solid samples were mounted on alumina sample holder and basal spacing (d-spacing) was determined via powder technique. Samples scans were carried out at 5-80° range with a scanning rate of 1°/ min.

The morphology of samples was analyzed by using field emission scanning electron microscope (FESEM). Samples were coated with a gold/palladium film, and the FESEM images were obtained using a secondary electron detector.

Preparation of the adsorbate solution

The dye used for the adsorption study was Reactive Red-141 and it was obtained from a local dyeing industry in commercial purity and used as such for the adsorption study without further purification. Molecular formula of the dye is $C_{52}H_{26}Cl_2N_{14}Na_8O_{26}S_8$ and molecular weight is 1774.19. The molecular structure of the dye is given in Fig. 1.

A stock solution of 1000 mg/L was prepared by dissolving 1000 mg of Reactive Red-141 dye in 1000 mL distilled water. The experimental solutions of the desired concentration 25, 50, 75 and 100 mg/L of RR-141 were prepared from stock solutions. All the chemicals used throughout this study were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. The initial pH is adjusted with 0.1 M HCl or 0.1 M NaOH was obtained by successive dilutions.

Batch adsorption experiments

The two synthesized adsorbents namely ZAC-LDH and CZA-LDH were used to carry out batch adsorption experiments. The optimized dose (except dose variation study) and volume of different initial concentration of RR-141 was agitated in an Orbital shaker (REMI make) at 170 rpm. The mixture was withdrawn at specified time intervals, centrifuged using electrical centrifuge (Universal make) at 5000 rpm for 20 min. The unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico BL198 Bio spectrophotometer at λ_{max} 546 nm. The effect of *p*H study was also performed by using dilute HCl and NaOH solutions. The effect of temperature was carried out at three different temperatures (30, 40 and 50°C). All experiments were carried out in duplicate for accuracy. The amount of dye at equilibrium (q_e) and at any time (q_t) on to two adsorbent was calculated using the following equation.

$$q_{e,t} = (C_0 - C_e) \times \frac{V}{m} \qquad \dots (1)$$

where $q_{e,\ t}$ (mg/g) is the adsorbed quantity at equilibrium (q_e) or at any time (q_t), C_0(mg/L) is the initial dye concentration, Ce,t(mg/L) is the dye concentration at equilibrium (C_e) or at any time (C_t), V (L) is the volume of the solution, and *m* (g) is the mass of the ZAC-LDH/CZA-LDH sample.

Regeneration of the adsorbents

Calcination was carried out in a muffle furnace at 450°C for 2 h in an air atmosphere with heating and cooling rates of 10°C/min to check the reusability of used ZAC-LDH and CZA-LDH material for the removal of RR-141. Then, the thermally regenerated material was reused for the removal of Reactive Red-141 dye from aqueous solution with the same adsorbent dosage (2g/L for ZAC-LDH and 0.5g/L for CZA-LDH) for 50 mg/L initial dye concentration.

Results and Discussion

Characterization

The characterization of the synthesized Zinc Aluminium carbonate LDH (ZAC-LDH) obtained by X-ray diffractogram showed that the phase corresponds to pure and original LDH materials[26] and was shown in Fig. 2 (a). The increased intensity and
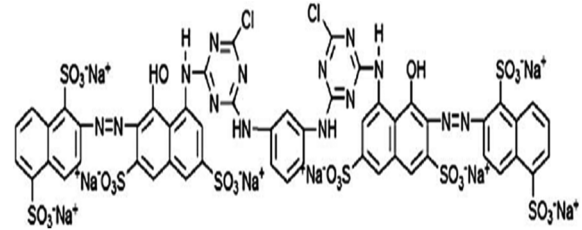

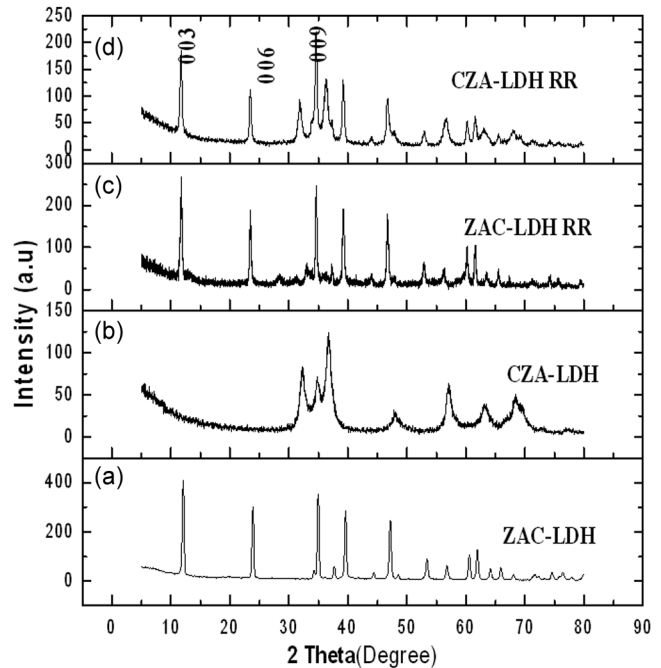Fig. 1 — Molecular structure of Reactive Red-141

Fig. 2 — XRD pattern of (a) ZAC-LDH; (b) CZA-LDH; (c) after adsorption of RR-141 onto ZAC-LDH (ZAC-LDH RR) and (d) after adsorption of RR-141 onto CZA-LDH (CZA-LDH RR)

the sharpness of the peak at lower 2θ value in diffractogram supported the solid consists of a well-crystallized single phase with large constituting crystallites. Furthermore, an intense reflection attributed to a secondary phases ZnO and Al(OH)$_3$ were seen around the higher 2θ value in the range of 35° – 60°. The crystalline ZnO is commonly obtained with the brukite-like layer[27,28].

On calcination of ZAC-LDH at 450°C, collapse the original layered structure with loss of inter layer carbonate anion, hydroxyl and water molecule with the formation of mixed metal oxide. The disappearance of basal reflections of planes (003) and (006) in XRD pattern in Fig.2 (b) confirms the loss of original layered structure with the formation of mixed metal oxides.

Figures 2 (a-d) are the XRD pattern of ZAC-LDH and CZA-LDH before and after dye adsorption. The dye adsorption by ZAC-LDH and CZA-LDH were mainly due to two mechanisms i.e., i) surface adsorption either by the formation of hydrogen bonding between OH⁻ and anion of dye molecule and or inter layer water molecule in ZAC-LDH with dye molecule. ii) Anion Exchange mechanism by intercalation of dye in the place of carbonate anion in the synthesized ZAC-LDH. This was confirmed by XRD pattern of both the adsorbents before and after adsorption of dye molecule which was shown in Fig. 2 (a-d)[29]. The adsorption of dye by CZA-LDH was actually due to the reconstruction of the original HT structure by intercalation of RR-141. This was further evidenced by reappearance of basal reflections of plane d(003) and d(006) in XRD Fig. 2(c). Thus it proves the RR-141 dye removal by both the adsorbents ZAC-LDH and CZA-LDH due to surface adsorption and anion-exchange mechanisms.
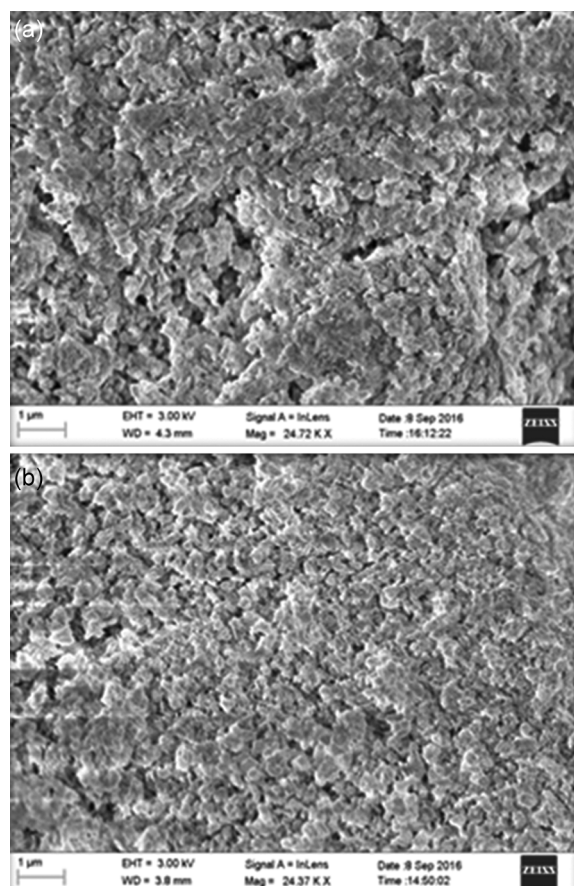
FESEM image of ZAC-LDH and CZA-LDH before and after adsorption of RR-141 are shown in Figs. 3 and 4 (a and b). It was evidenced that the surface coverage by the dye molecule in Fig. 3 (b) and heterogeneity occurrence in Fig. 4 (b) proved the adsorption of RR-141 by both the adsorbents.

Effect of agitation time and initial dye concentration

Adsorption experiments were carried out at different initial dye concentrations ranging from 25 to 100 mg/L at 30°C. The amount of RR-141 dye removal was increased with contact time by the adsorbent ZAC-LDH and CZA-LDH. The adsorption efficiency was increased due to increase in the availability of active sites on the adsorbents when increasing the initial dye concentration[30]. It was evident that the maximum amount of 22.50 mg/g and 44.67 mg/g of dye was adsorbed for 50 mg/L initial dye concentration at the contact time of 80 min by ZAC-LDH and 90 min by CZA-LDH respectively.
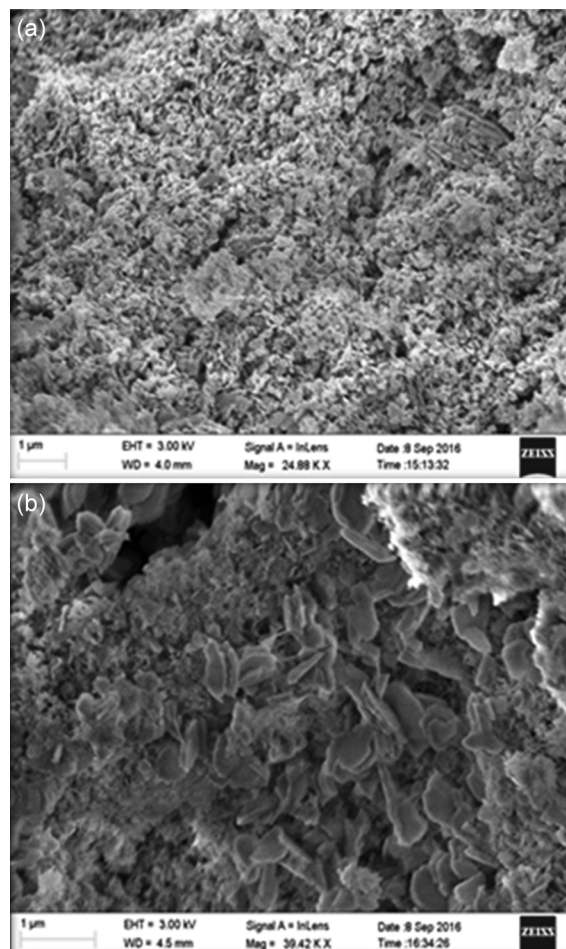

Fig. 3 — FESEM image of ZAC-LDH (a) Before adsorption of RR-141and (b) After adsorption of RR-141

Fig. 4 — FESEM image of CZA-LDH (a) Before adsorption of RR-141and (b) After adsorption of RR-141

After this, both the curves were reached equilibrium and beyond this continue with no significant change in the extent of adsorption. From the Fig. 5 (a & b), it was observed that the percentage of dye removal was decreased from 92.11 % to 82.41 % for ZAC-LDH and 93.94 % to 82.41 % for CZA-LDH while increasing the initial dye concentrations from 25 to 100 mg/L. This shows that the adsorption was highly dependent on initial concentration of dye. At lower concentration, the sites availability on adsorbents is more for adsorption than at high concentration and hence the percentage of dye removal was decreased with increase of initial dye concentration.

Effect of temperature

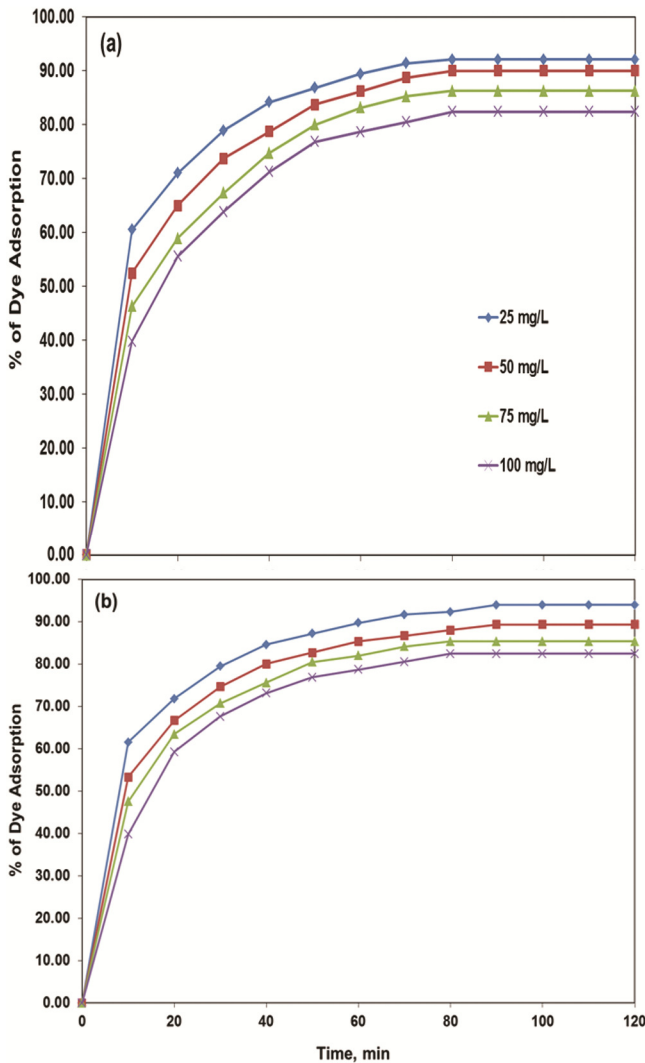To investigate the effect of temperature for the removal of RR-141 by ZAC-LDH and CZA-LDH, the experiments were carried out at three different temperatures (30, 40 and 50°C). As the solution temperature strongly affects the adsorption efficiency of RR-141, the percentage removal of RR-141 by ZAC-LDH and CZA-LDH was increased from 90% to 95% and 89.33% to 93.33% respectively for the initial dye concentration 50 mg/L on increasing the temperature from 30°C to 50°C. This proved that the adsorption of RR-141 was endothermic for both adsorbents.

Effect of *p*H

The solution *p*H is an important parameter that affects adsorption of dye molecules[31]. The effect of *p*H on the adsorption of RR-141 by ZAC-LDH and CZA-LDH were investigated with varying the initial *p*H of dye (initial dye concentration - 50 mg/L) between 2 and 12. The point zero charge of adsorbent was an important one to explain the effect of pH for the dye removal. The PZC of ZAC-LDH and CZA-LDH was found to be 8.07 and 8.6 respectively. The percentage of dye removal was more at *p*H<PZC and less at *p*H>PZC by ZAC-LDH and CZA-LDH. At pH<PZC, the positive charge on both the LDH surface causes electrostatic attraction between anionic dye and positively charged LDH surface causes increase in the percentage of dye removal whereas at *p*H>PZC, the electrostatic repulsion of deprotonated adsorbent of ZAC-LDH & CZA-LDH surface and dye anion results decrease in the rate of adsorption. At acidic *p*H 2, the maximum dye removal of 100% for ZAC-LDH and 80% for CZA-LDH was observed and was shown in Fig. 6.
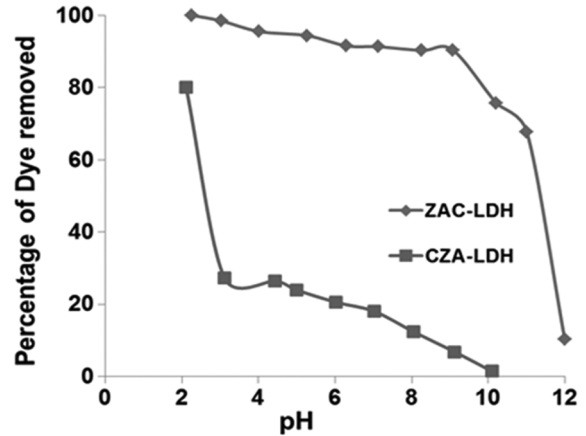

Fig. 5 — Effect of initial dye concentration on the adsorption of RR-141 by (a) ZAC-LDH and (b) CZA-LDH

Fig. 6 — Effect of *p*H on the removal of RR-141 dye by ZAC-LDH and CZA-LDH
(Initial Conc -50 mg/L; Temp-30°C)

Effect of adsorbent dose

The effect of adsorbent dose for the removal of RR-141 by ZAC-LDH and CZA-LDH was carried out with 50 mg/L initial dye concentration. The removal of dye was increased with increment of adsorbent dose. This was due to the increase in the active sites on the adsorbent surface by incremental addition of adsorbents and thus making the easy penetration of dye molecule onto adsorbent site[32]. The maximum dye removal was found to be 95.38% by ZAC-LDH and 89.33% by CZA-LDH with the adsorbent dose of 2 g/L and 0.5 g/L respectively. Beyond this, addition of further adsorbent dosage does not cause any improvement in the adsorption process for both the adsorbents.

Kinetics studies

Pseudo-first order model

In order to design the model and mechanism of adsorption processes such as transfer and chemical reaction, three kinetic models i.e., pseudo-first order[33], pseudo-second order[34] and intraparticle diffusion models were applied for the adsorption of RR-141 dye onto both adsorbents such as ZAC-LDH and CZA-LDH. The pseudo-first order rate equation proposed by Lagergren [35] is

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad \cdots (2)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium and time t (min), k_1 is the pseudo first order rate constant (min^{-1}). The value of q_e and k_1 is calculated from intercept and slope of the plot log $(q_e$-$q_t)$ vs time for different initial concentrations and different temperatures for both adsorbents. The calculated values were summarized in Table 1 (a and b). From the correlation coefficient R^2 value, it is clear that pseudo first order equation does not fit well for both the adsorbents for the whole range of initial dye concentrations studied.

Pseudo-second order model

The pseudo-second order kinetic equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad \cdots (3)$$

The values of k_2 second order rate constant (g/mg/min) and q_e equilibrium adsorption capacity (mg/g) can be calculated from the plot of t/qt versus t for different initial concentration (25, 50, 75 and 100 mg/L) and

temperature (30, 40 and 50°C). The pseudo-second order kinetic model for both the adsorbent for different initial concentration was shown in Fig. 7. The calculated kinetic parameters k_2 and q_e from the intercept and slope of the plot were given in Table 1 (a and b). The calculated rate constant k_2 value decreases with increase in initial dye concentration. The correlation coefficient (R^2) values are greater than 0.998 indicates that the adsorption of RR-141 by both the adsorbents ZAC-LDH and CZA-LDH fits well to the pseudo-second order kinetics model than pseudo-first order kinetic model for all concentrations[36].

Intraparticle diffusion model

Since the pseudo-first order and pseudo-second order kinetic models could not identify the diffusion mechanism, the intraparticle diffusion approach can be used to predict if intra-particle diffusion is the rate-limiting step. The kinetic results were analyzed by using the intraparticle diffusion model to elucidate the diffusion mechanism. Vigorous agitation of the
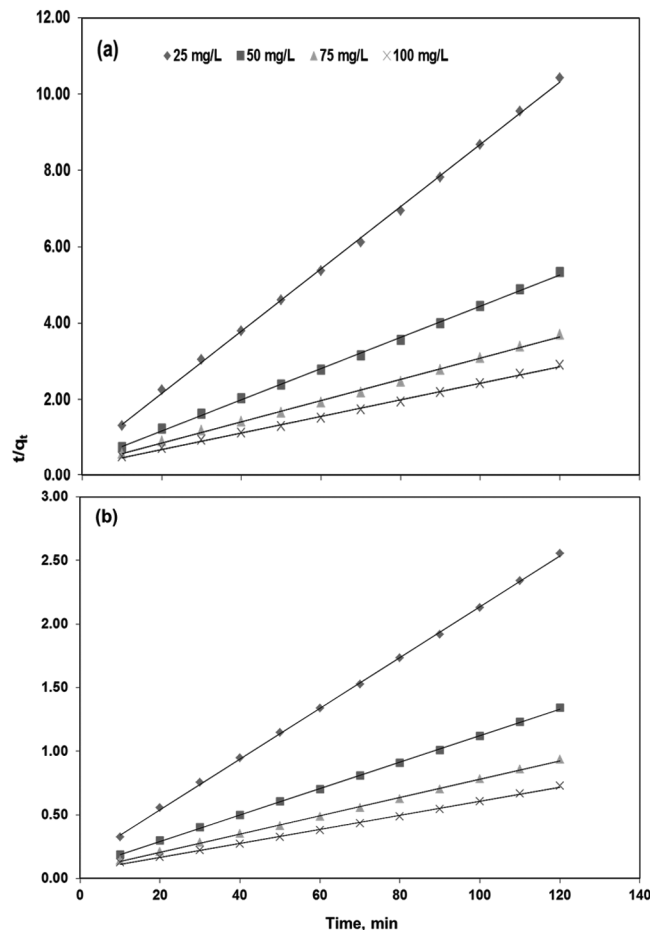

Fig. 7 — Pseudo-second order kinetics model for the removal of RR-141 by (a) ZAC-LDH and (b) CZA-LDH

Table 1 (a) — Kinetic parameters for the adsorption of RR-141 by ZAC-LDH and CZA-LDH for different
initial dye concentration at temperature 30°C

Adsorbents	ZAC-LDH				CZA-LDH			
	Initial Concentration (mg/L)							
Parameter	25	50	75	100	25	50	75	100
q_e exp (mg/g)	11.51	22.50	32.37	41.20	46.97	89.33	128.05	164.81
	Pseudo-first order kinetics model							
k_1 (min^{-1})	0.055	0.055	0.058	0.053	0.042	0.047	0.056	0.052
q_e cal (mg/g)	10.12	20.50	33.91	40.19	33.39	66.77	114.95	146.99
R^2	0.9624	0.9764	0.9731	0.995	0.9765	0.9841	0.986	0.9958
	Pseudo-second order kinetics model							
k_2 (g/mg min^{-1})	0.013	0.005	0.003	0.002	0.003	0.001	0.001	0.001
h	1.896	2.735	3.333	3.876	6.978	11.737	16.129	17.637
q_e cal (mg/g)	12.27	24.51	35.97	46.30	50.25	96.15	138.89	181.82
R^2	0.9994	0.999	0.9981	0.998	0.9997	0.9997	0.9991	0.9985
	Intraparticle diffusion model							
k_{id} (mg/g/min$^{1/2}$)	2.107	0.876	0.539	0.395	0.507	0.237	0.154	0.106
R^2	0.8432	0.8614	0.858	0.8424	0.8824	0.8596	0.8278	0.8055

Table 1(b) — Kinetic parameters for the adsorption of RR-141 by ZAC-LDH and CZA-LDH at different temperatures
(initial dye concentration of 50mg/L)

Adsorbents	ZAC-LDH			CZA-LDH		
	Temperature °C					
Parameter	30	40	50	30	40	50
q_e exp (mg/g)	22.50	23.13	23.75	89.33	92.00	93.33
	Pseudo-first order kinetics model					
k_1 (min^{-1})	0.055	0.055	0.056	0.047	0.046	0.055
q_e cal (mg/g)	20.50	18.94	18.13	66.77	64.30	70.49
R^2	0.9764	0.9811	0.9812	0.9841	0.975	0.9826
	Pseudo-second order kinetics model					
k_2 (g/mg min^{-1})	0.00455	0.00557	0.00651	0.00127	0.00137	0.00162
h	2.735	3.432	4.129	11.737	13.210	15.924
q_e cal (mg/g)	24.51	24.81	25.19	96.15	98.04	99.01
R^2	0.999	0.999	0.9995	0.9997	0.9997	0.9995
	Intraparticle diffusion model					
k_{id} (mg/g/min$^{1/2}$)	0.876	0.970	1.090	0.237	0.251	0.271
R^2	0.8614	0.8478	0.8614	0.8596	0.8783	0.8536

solution mixture during the experiment may results the transport of adsorbate ion from the solution into the pores of adsorbent which is the rate limiting step. The intra particle diffusion model is expressed as

$$q_t = k_{id} \, t^{1/2} + C \qquad \dots (4)$$

The possibility of intraparticle diffusion was tested by plotting a graph between the amount of dye adsorbed q_t and $t^{1/2}$ at different time intervals for different concentrations. The values of k_{id} for all concentrations at 30°C and for different temperatures for 50 mg/L initial dye concentration were determined from the slopes of plots. The intraparticle diffusion plot was not passed through the origin, the adsorption of RR-141 by ZAC-LDH and CZA-LDH was

followed the boundary layer diffusion to some extent only not to the whole range[37].

Adsorption isotherm

Adsorption isotherm is an important parameter to analyze the equilibrium relation between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at constant temperatures. In this study, Langmuir[38] and Freundlich[39] isotherm models were used to interpret the adsorption equilibrium of RR-141 by ZAC-LDH and CZA-LDH.

Langmuir isotherm

The Langmuir adsorption isotherm is the best known linear model for monolayer adsorption on the homogeneous surface and most frequently utilized to

Table 2 — Isotherm parameters for adsorption of RR-141 by ZAC-LDH and CZA-LDH

Sample	Temperature °C	Isotherm Models						
		Langmuir				Freundlich		
		Q_0	b	R_L	R^2	n	k_f	R^2
ZAC-LDH	30	62.50	0.0074	0.7304	0.9971	1.612	7.053	0.988
	40	63.29	0.0074	0.7311	0.9988	1.598	7.561	0.9843
	50	67.11	0.0070	0.7405	0.9969	1.566	8.368	0.9889
CZA-LDH	30	59.17	0.0078	0.7187	0.9981	1.662	7.290	0.9858
	40	60.61	0.0077	0.7216	0.9947	1.650	7.927	0.9835
	50	59.17	0.0080	0.7144	0.9975	1.695	9.012	0.9774

determine the adsorption parameters. Langmuir model is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b_L} + \frac{C_e}{Q_0} \qquad \ldots (5)$$

where, C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 and b_L are constants related to monolayer adsorption capacity and energy of adsorption (L/mg). The calculated values are summarized in Table 2. Langmuir dimensionless constant R_L value lies between 0 and 1 indicates that the adsorption nature is favourable. The plot of C_e/q_e against C_e gave a straight line with slope $1/Q_0$ and intercept with b shown in Fig. 8. The maximum monolayer coverage capacity (Q_0) from Langmuir Isotherm model was found to be 62.50 mg/g and 59.17 mg/g at 30°C for ZAC-LDH and CZA-LDH respectively. Langmuir model is more appropriate to explain the nature of adsorption of RR-141 with high correlation coefficient (R^2).

Freundlich model

The Freundlich isotherm is an empirical equation employed to describe the multilayer adsorption and adsorption on heterogeneous systems. The linearized form of Freundlich equation can be written as

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad \ldots (6)$$

where k_f is the measure of adsorption capacity and n is the adsorption intensity and are calculated from intercept and slope of a linear plot of log q_e versus log C_e. The value of 1/n is lower than one for adsorption of RR-141 dye onto ZAC-LDH and CZA-LDH indicating that the adsorption of RR-141 by both the adsorbent material was favourable. More over
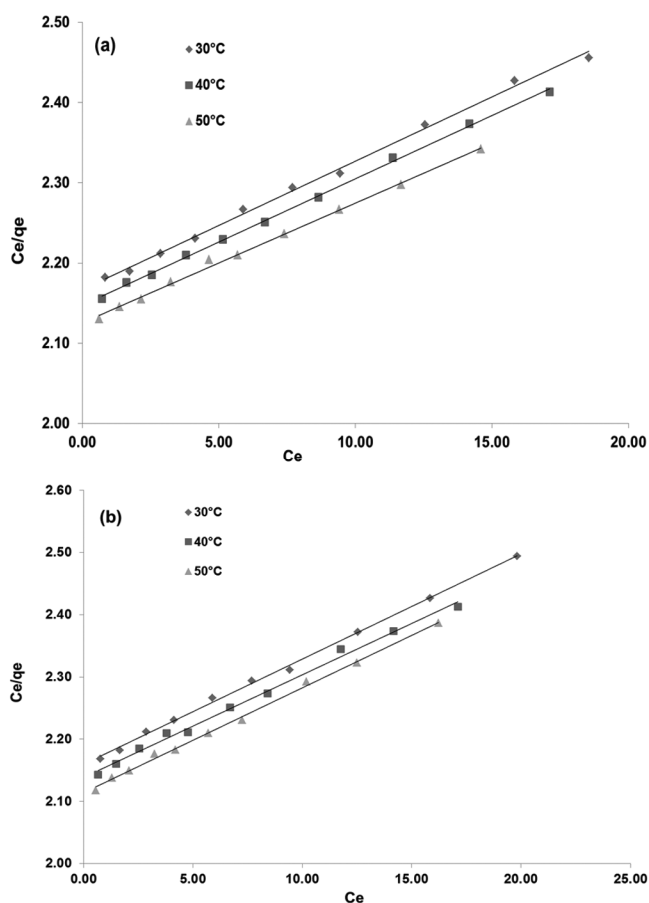

Fig. 8 — Langmuir isotherms for adsorption of RR-141 by (a) ZAC-LDH and (b) CZA-LDH

equilibrium data fitted well to the Freundlich isotherm with high correlation coefficient value (R^2). The higher correlation coefficients value for the Freundlich isotherm predicts heterogeneity and multilayer adsorption of RR-141 by both the adsorbent shown in Table 2. The correlation coefficient shows that the Freundlich model is comparable to Langmuir model and the value of 1/n is less than 1 indicates that the adsorption of RR-141 onto both the adsorbents ZAC-LDH and CZA-LDH is favourable.

Thermodynamic parameters

Thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) of adsorption were calculated from the following equations was given in Table 3.

$$\Delta G^0 = -RT \ln K_c \qquad \ldots (7)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad \ldots (8)$$

where K_c is the standard thermodynamic equilibrium constant and T is the absolute temperature. The ΔH^0 values were calculated from the slopes of linear variation of lnK versus 1/T and the results are summarized in Table 3. The positive **ΔH^0** value for the adsorption of RR-141 by the adsorbents ZAC-LDH and CZA-LDH suggested that the adsorption process was endothermic in nature. And it was further supported by the increase of dye adsorption by increasing the temperature. The enthalpy value **ΔH^0** is used to distinguish the physical and chemical adsorption[40,41]. Generally enthalpy change ΔH^0 values between 40–120 KJ /mol shows chemisorption and below 40 KJ/mol shows physisorption[42]. Here the calculated value of **ΔH^0** for the adsorption of RR-141 by both the adsorbents lies below 40 KJ/mol which indicates that both the adsorption processes are physisorption. The negative value of ΔG^0 indicates the high affinity of RR-141dye to the surface of ZAC-LDH and CZA-LDH and also spontaneous nature of adsorption process. Furthermore, 0000000000the positive ΔS^0 values indicated that the degrees of freedom increased at the solid – liquid interface during adsorption of the reactive dye. Similar thermodynamic results were reported for the removal of anionic dyes by Layered double hydroxides[43-45].

Reusability of the adsorbents

In order to analyze the reusability of the adsorbent, thermal regeneration was carried out in a muffle furnace at 450°C for 2 h in an air atmosphere with heating and cooling rates of 10°C/min for each cycle. The calcined material of both adsorbents were used for the removal of RR-141 dye from aqueous solution with adsorbent dose of 2.0 g/L for ZAC-LDH and 0.5 g/L for CZA-LDH for 50 mg/L initial dye concentration. Three reusability cycles were performed to understand the efficiency and reusability

Table 3 — Thermodynamic parameters from Van't Hoff plots for the adsorption of Reactive Red dye (RR-141) by ZAC-LDH and CZA-LDH at different temperature

Adsorbent	Temperature °C	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/K/mol)
ZAC-LDH	30	-5.54	30.34	118.21
	40	-6.54		
	50	-7.91		
CZA-LDH	30	-5.36	21.35	88.27
	40	-6.36		
	50	-7.12		

of the materials for the removal of RR-141 from aqueous solution. Successive decrease in dye removal was observed for both adsorbents on increasing the recycling process. In the third cycle, the percentage of dye removal was found to be 52.94% and 41.18% for regenerated ZAC-LDH and CZA-LDH respectively. This decrease was mainly due to the loss of original LDH structure on successive calcination of LDH.

Conclusion

The present study shows that the prepared two adsorbent materials such as ZAC-LDH and CZA-LDH can be employed for the effective removal of Reactive Red -141(RR-141) from aqueous solution. The amount of dye adsorbed is found to increase from 11.51 - 41.20 mg/g and 46.97 - 164.81 mg/g for ZAC-LDH and CZA-LDH respectively with increase in the initial dye concentration from 25 - 100 mg/L. The increase in the amount of adsorption of dye with increase in temperature from 30- 50°C indicates that the process is endothermic in nature, which is further confirmed by positive **ΔH^0** values. From the performed kinetic models, pseudo-second-order kinetic model is more fit than the pseudo first order kinetic model with high correlation coefficient R^2 value (>0.998) for the removal of RR-141. The optimum *p*H for maximum dye removal is found to be 100 % for ZAC-LDH and 80% for CZA-LDH at highly acidic *p*H 2. Both Langmuir and Freundlich isotherm model describe the adsorption mechanism of dye by both the adsorbents with high correlation coefficient (R^2) value. The result of reusability of the adsorbents up to third cycle is remarkable. The XRD pattern confirm that the adsorption and intercalation of RR-141 dye molecule onto the adsorbent ZAC-LDH and CZA-LDH. The thermodynamic parameters like ΔG°, ΔH° and ΔS° were also evaluated and indicated that the adsorption process was spontaneous and endothermic in nature.

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