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Comparative studies on the adsorptive removal of Acid Violet-17 dye from aqueous solution by using zinc aluminium carbonate-LDH (ZAC-LDH) and modified LDH

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ABSTRACT

Removal of Acid Violet-17 (AV-17) from aqueous solution by using different adsorbents such as zinc aluminium carbonate–layered double hydroxide (ZAC-LDH) and its calcined sample (CZA-LDH) were studied through batch adsorption process. This study was carried out with different variables include contact time, initial dye concentration, pH, sorbent dose, and temperature. The pseudo-second-order kinetic model describes the kinetics of AV-17 adsorption by both ZAC-LDH and CZA-LDH with high correlation coefficient when compared with pseudo-first-order model. The equilibrium data was examined using Langmuir and Freundlich isotherm models. The Freundlich isotherm model described the heterogeneity and multilayer adsorption of dye by both the adsorbent. The optimum pH for the maximum adsorption of AV-17 dye was found to be 96.9% for ZAC-LDH and 99.06% for CZA-LDH at acidic pH = 3. The maximum adsorption capacities for the removal of AV-17 onto ZAC-LDH and CZA-LDH were found to be 114.94 and 454.55 mg/g at 30°C, respectively. The X-ray diffraction pattern of CZA-LDH before and after the adsorption emphasizes that the dye adsorption was significantly enhanced by reconstruction of its original layered structure by the intercalation of AV-17 dye molecule with memory effect. These results prove that the synthesized CZA-LDH was more efficient than the ZAC-LDH. The calculated thermodynamic parameters like ΔG° and ΔH° reveal that the adsorption process is spontaneous and endothermic in nature. The calculated Langmuir dimensionless separation factor R_L and n value of the Freundlich equation also supports the favourability of the adsorption process. Thermal regeneration and reusability of ZAC-LDH and CZA-LDH up to three cycles are remarkable for the removal of AV-17 dye. These results emphasize that the calcined product CZ-LDH is found to be a suitable adsorbent for AV-17 dye from aqueous solution.

Keywords: Layered double hydroxide; Langmuir separation factor; Kinetics; Thermodynamics; Acid Violet-17 dye

1. Introduction

Synthetic dyes have been used widely in various industrial sectors like textile, dye houses, paper printers, leather, cosmetics etc. The effluents from these industries, especially from textile industries, carry a large number of dyes and other degraded products during the colouring process [1]. Even the trace amount of dyes in water is highly visible and undesirable [2]. The release of this coloured wastewater is hazardous for the aquatic life in terms of hindering photosynthetic activity. Many of the dyes used in our daily routine are carcinogenic, mutagenic and also toxic to all lives and environment. Sometimes, the dyes may also undergo degradation to form highly toxic and carcinogenic products [3]. These toxic dyes have significant impact on the human health and the aquatic life [4]. Therefore, various attempts were made for the treatment of wastewater

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from textile industries. Several methods were exported for the treatment of dyes and toxic molecules from wastewater stream including coagulation, flocculation, precipitation [5], ozonation [6], oxidation [7], photocatalysis [8] etc. Recent technologies such as electro chemical treatment, solvent extraction, membrane filtration and advanced oxidation process have also been used for the removal of dyes from wastewater. Due to low biodegradability, the conventional methods were not considered efficient, while the adsorption process has proven to be an effective process for the removal of dyes and heavy metals because of its simplicity and cost-effective operation [9]. Many researchers have employed various adsorbents prepared from waste materials such as orange peel [10], banana peel [11], lemon peel [12], raw barley straw [13], egg shell [14], sawdust [15], rice husk [16], fly ash [17,18], wollastonite [19,20], coir pith carbon [21], tea waste [22], sugarcane bagasse [23,24], peanut husk [25,26], bottom ash [27], multi-walled carbon nanotubes/ThO_2 nanocomposite [28], L-cysteine-modified montmorillonite-immobilized alginate nanocomposite [29], iron oxide-impregnated dextrin nanocomposite [30], poly (methyl methacrylate)-grafted alginate/Fe_3O_4 nanocomposite [31], *Hibiscus cannabinus* fibre [32] etc., for the removal of dyes and toxic substances from water and wastewater [33].

Among the different adsorbents, layered double hydroxides received much attention in the last few years due to their vast applicability such as adsorption, catalyst, nanotechnology and biotechnology [34–39]. The general formula of layered double hydroxide (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.) [40,41]. Carbonates are the interlayer anion present in naturally occurring mineral hydroxide, which is a member of this class of materials. Co-precipitation is usually used for the preparation of pure LDH, in which solution containing metals are mixed with a basic solution such as NaOH for precipitation and Na_2CO_3 for providing CO_3^{2-} interlayer anion. Because of the superior property like anion exchange ability, large surface area and regeneration ability, LDH finds wide application in wastewater treatment as an adsorbent and photocatalyst [42].

The aim of the present study is to synthesize zinc aluminium carbonate LDH (ZAC-LDH) by co-precipitation followed by hydrothermal method at 120°C using cetyl trimethyl ammonium bromide (CTAB) as soft template. The synthesized ZAC-LDH is calcined at 450°C in a muffle furnace to about 2 h in an air atmosphere with heating and cooling rates of 10°C/min. The ZAC-LDH and its calcined product (CZA-LDH) are employed as an adsorbent to investigate the AV-17 dye removal from aqueous solution. Taking the advantage of the "memory effect" for the LDH materials, the CZA-LDH with higher uptake capability is explained due to reconstruction of the original layered structure in an aqueous solution containing intercalation anion AV-17 from aqueous solution.

2. Materials and methods

2.1. Preparation of ZAC-LDH and CZA-LDH

ZAC-LDH was synthesized by using aqueous solution of $ZnSO_4.7H_2O$ and $Al_2(SO_4)_3.16H_2O$. The aqueous solution of zinc sulphate (1 M) and aluminium sulphate (1 M) was taken in the molar ratio $M^{2+}/M^{3+} = 3$ and mixed in magnetic stirrer. Exactly 0.3 g of the CTAB was added to the solution and made the solution as a homogeneous mixture with a magnetic stirrer. Precipitating agent sodium hydroxide (1 M) and intercalating carbonate anion source sodium carbonate (0.5 M) mixture were added dropwise 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. And 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 in this article. The calcined ZAC-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.

2.2. 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 A°) at 40 kV and 200 mA. Solid samples were mounted on alumina sample holder, and basal spacing (d-spacing) was determined via powder technique. Scanning of samples were carried out at 5°–80° range with a scanning rate of 1°/min.

2.3. Adsorbate

Acid Violet-17 (AV-17) dye was obtained from a local dyeing industry (manufacturing company) in commercial purity and used as such for the adsorption study without further purification. Molecular formula of the dye is $C_{41}H_{48}N_3NaO_6S_2$ with colour index: 42650 and molecular weight: 765.96. The structure of AV-17 was shown in Fig. 1.

A stock solution of 1,000 mg/L of the dye was prepared by dissolving appropriate quantity of dye in double distilled water, and the experimental solutions of the desired concentration (25–100 mg/L) were obtained from the stock solution by successive dilutions. All chemicals used were of analytical reagent grade (Merck/SRL, India). Double distilled water was used throughout the study.

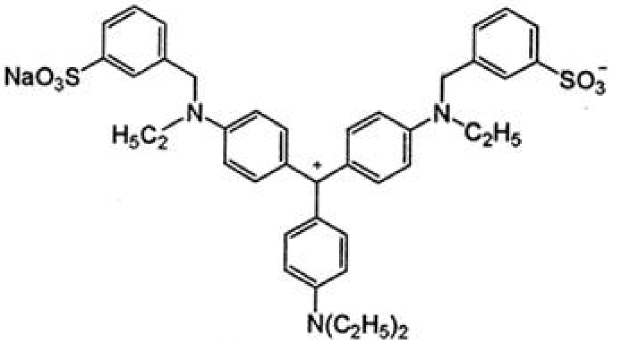

Fig. 1. Structure of Acid Violet-17 (AV-17).

2.4. Batch adsorption experiments

Absorbance of 10 mgL^{-1} was determined at different wavelengths using UV visible spectrophotometer to obtain a plot of absorbance vs. wavelength. The wavelength corresponding to the maximum absorbance (λ_{max} = 545 nm) as determined from the plot was noted. This wavelength was used for measuring the absorbance of residual concentration of AV-17. The efficiency of an adsorbent ZAC-LDH and CZA-LDH was evaluated by conducting batch mode experiments. The experiment was carried out by using different experimental conditions by varying initial dye concentrations (25–100 mg/L) of AV-17 dye solution, contact time, pH and temperature. The mixture was withdrawn at specified intervals and centrifuged by electrical centrifuge at 5,000 rpm for about 15 min. The residual dye concentration of unadsorbed supernatant liquid was analyzed for the using Elico BL198 biospectrophotometer at λ_{max} = 545 nm.

The adsorbed amounts at equilibrium (q_e) and at any time (q_t) were calculated using the following equation:

$$q_{e,t} = \left(C_0 - C_e\right) \times \frac{V}{m} \times M \tag{1}$$

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; $C_{e,t}$ (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.

The pH of solutions was adjusted using 1 M HCl and 1 M NaOH. The pH metre was used to adjust the pH of dye solution as per the requirement. The effect of temperature was also studied at 30°C, 40°C and 50°C. All experiments were carried out in duplicate for accuracy.

2.5. Regeneration of the adsorbents

Regeneration of the adsorbent was carried out by calcination of used material ZAC-LDH and CZA-LDH in a muffle furnace at 450°C for 2 h in an air atmosphere with heating and cooling rates of 10°C/min. Then the regenerated material was reused for the removal of AV-17 dye from aqueous solution with the same adsorbent dosage (2 g/L for ZAC-LDH and 0.5 g/L for CZA-LDH) for 50 mg/L initial dye concentration.

3. Results and discussion

3.1. Characterization

The XRD patterns of synthesized ZAC-LDH fitted well with the characteristic reflections of regular layered structure of LDH materials [43]. The basal reflections of planes hkl (003), (006), (012), (015), (110) and (113) were also resembled the previous study [44]. High crystallinity of the synthesized material was supported by the increased intensity and the sharpness of the peak at lower 2θ value from XRD pattern. Furthermore, an intense reflection attributed to a secondary phases ZnO and $Al(OH)_3$ was seen around the higher 2θ value in the range of 35°–60°. The crystalline ZnO is commonly obtained with the brukite-like layer [45,46].

On calcination of ZAC-LDH at 450°C, collapse the original layered structure with loss of interlayer carbonate anion, hydroxyl and water molecule with the formation of mixed metal oxide. The XRD pattern of CZA-LDH shows the formation of mixed metal oxides. The dye adsorption by ZAC-LDH was mainly due to two mechanism, i.e., (i) the formation of hydrogen bonding between OH^- and anion of dye molecule and water in the interlayer of ZAC-LDH and (ii) the dye removal was due to incomplete intercalation of dye by ion exchange process with carbonate anion in the synthesized ZAC-LDH. This is confirmed by shifting of basal reflection d (003) to lower 2θ value 11.527° from 12.065° and also causes slight increase in interlayer distance between the metal ions from 7.330 to 7.676 Å compared with original ZAC-LDH [47]. Further, the enhanced dye removal by CZA-LDH was attributed by the reconstruction of original layered structure of CZA-LDH by the intercalation of anionic dye AV-17 from aqueous solution with “memory effect”.

3.2. Effect of initial dye concentration and contact time

The experimental results of adsorptions of AV-17 onto ZAC-LDH and CZA-LDH at various initial concentrations (25, 50, 75 and 100 ppm) with contact time of 2 h were studied, and the amount of AV-17 adsorbed/unit mass of ZAC-LDH and CZA-LDH adsorbent was increased with increase of initial dye concentration for fixed contact time of 2 h was shown in Fig. 2. The rapid adsorption observed during the initial stage of the study was probably due to the abundant availability of active sites on the surface and reached equilibrium at about 70 min for both the adsorbents. In this study, the adsorption capacity at equilibrium (q_e) increases from 11.78 to 42.48 mg/g for ZAC-LDH and from 48.08 to 172.55 mg/g for CZA-LDH with an increase in the initial dye concentrations from 25 to 100 mg/L. This shows that the adsorption is highly dependent on initial concentration of dye. It is because of that at lower concentration, the available surface area is more when compared with high concentration. However, at high concentration, the available sites of adsorption become lesser, and hence, the percentage removal of dye gets decreased with increase in initial dye concentration.

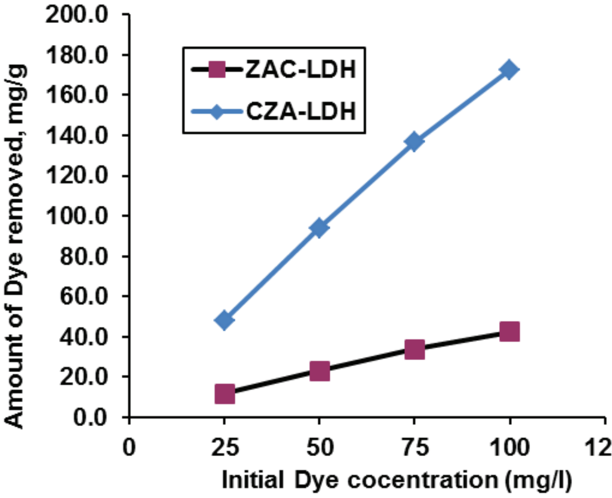

Fig. 2. Effect of initial dye concentration on the adsorption of AV-17 by ZAC-LDH and CZA-LDH.

3.3. Effect of pH

The pH is one of the most important factor that controlling the adsorption of dye onto the adsorbent [48]. The amount of dye adsorption of AV-17 dye onto ZAC-LDH and CZA-LDH at different initial solution pH was carried out by varying the solution pH between 2 and 11. Since the point of zero charge (PZC) 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 determined by following the procedure described by Sharma et al. [49]. It was found to be 8.07 and 8.6 for ZAC-LDH and CZA-LDH, respectively. The PZC can be used as a qualitative parameter for the adsorbent surface charge balance. Fig. 3 clearly shows that the optimum pH for the maximum dye removal of 96.9% for ZAC-LDH and 99.06% for CZA-LDH occurred at acidic pH = 3, respectively. At pH < PZC, the adsorption of dye may be due to two possible mechanism, i.e., one was anionic exchange of CO_3^{2-} anion in the interlayer by dye anion SO_3^-, and the other one is adsorption of dye anion SO_3^- by protonated positively charged ZAC-LDH surface and CZA-LDH. But at the same time, decrease of dye removal was observed at pH > PZC due to repulsion between the deprotonated adsorbent of ZAC-LDH and CZA-LDH surface and dye anion. Actual colour of AV-17 was changed to colourless after the pH = 9 results unusual behaviour in the AV-17 dye removal by CZA-LDH.

3.4. Effect of adsorbent dose

The effect of adsorbent dose for the removal of AV-17 onto ZAC-LDH and CZA-LDH is shown in Fig. 4. There is an increase in adsorption with the increment of adsorbent dose for 50 mg/L initial dye concentration, and this is attributed by the increased surface area and availability of more adsorption sites.

The efficiency of dye removal was 92.17% using 2 g/L of ZAC-LDH compared with 81.74% using 0.5 g/L. But at the same time 93.91% removal of AV-17 dye was achieved by four times reduction in adsorbent dose of 0.5 g/L of CZA-LDH. Since there was no significant change in the dye removal after 2 g/L for ZAC-LDH and 0.5 g/L for CZA-LDH was due to attainment of equilibrium between the adsorbate and adsorbent [50]. This result emphasized the optimum dose of both adsorbent for further study.

3.5. Adsorption kinetics

The prediction of the adsorption kinetics of dye from aqueous system is very important to design a suitable treatment system. In order to analyze the adsorption kinetics of AV-17 dye by ZAC-LDH and CZA-LDH, the following kinetic equations have been studied.

3.5.1. Pseudo-first-order kinetics

The first-order equation is the simplest one and is the most widely used equation for the adsorption of a solute from a solution. The integrated linear form of pseudo-first-order equation [51] is as follows:

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

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 for both adsorbents are shown in Figs. 5(a) and (b).

The calculated values are summarized in Table 1. The pseudo-first-order kinetic model is poorly fit with adsorption data as the correlation coefficient value (R^2) is low. Hence, the adsorption does not follow first-order rate expression.

3.5.2. Pseudo-second-order kinetics

Adsorption of dyes on adsorbent materials has been observed that evolution of the adsorbed amount with time follows second-order law:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

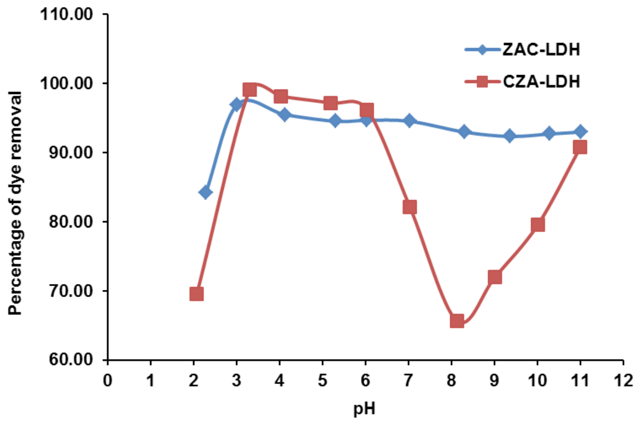

Fig. 3. Effect of initial pH on the adsorption of AV-17 by ZAC-LDH (C_0 = 50 mg/L, T = 30°C, and dosage 2 g/L for ZAC-LDH and 0.5 g/L for CZA-LDH).

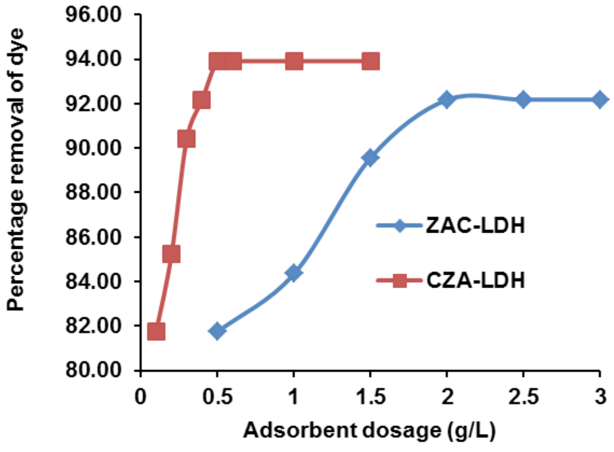

Fig. 4. Effect of dosage of ZAC-LDH and CZA-LDH for the removal of AV-17.

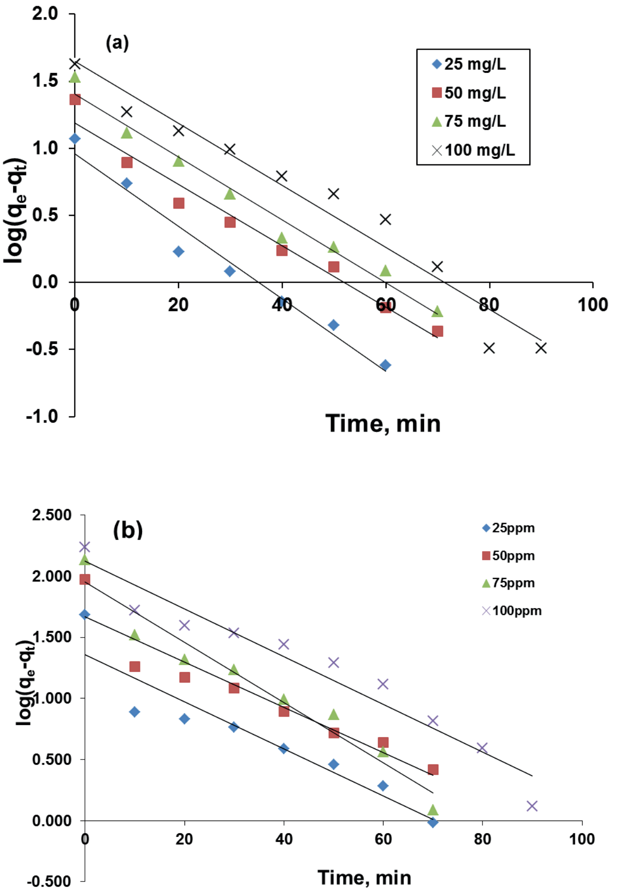

Fig. 5. Pseudo-first-order kinetics for adsorption of AV-17 by: (a) ZAC-LDH and (b) CZA-LDH.

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/q_t vs. t for different initial concentration and temperature are shown in Fig. 6. The results of second-order plot are given in Table 1. The correlation coefficient (R^2) values are greater than 0.9989. These result shows that the adsorption of AV-17 dye onto both the adsorbent ZAC-LDH, and CZA-LDH follows the second-order kinetics that describes the adsorption much better than pseudo-first-order kinetics. The maximum adsorption capacities q_e calculated from pseudo-second-order model for both adsorbent ZAC-LDH and CZA-LDH were in accordance with the q_e experimental values [52]. This confirmed that the adsorption obeys pseudo-second-order kinetics than the pseudo first order for both adsorbent. The linear fit of pseudo second order supported that chemisorption is the rate-determining step of the adsorption process [53].

3.6. Adsorption isotherm

3.6.1. Langmuir model

The adsorption isotherms are generally used for designing the adsorption system. The linear equations of Langmuir and Freundlich isotherms are employed to design the adsorption system of AV-17 by ZAC-LDH and CZA-LDH. The linear equation of Langmuir is given in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b_L} + \frac{C_e}{Q_0} \tag{4}$$

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); and Q_0 and b_L are constants related to

Table 1
Kinetic parameters for adsorption of AV-17 by ZAC-LDH and CZA-LDH

Sample	Concentration, T°C		$q_{e,\exp}$ (mg/g)	Pseudo-first-order kinetics model			Pseudo-second-order kinetic model			
				k_1 (min^{-1})	$q_{e,\text{cal}}$ (mg/g)	R^2	k_2 (g/mg min^{-1})	h	$q_{e,\text{cal}}$ (mg/g)	R^2
ZAC-LDH	Conc.	25 mg/l	11.78	0.0546	6.23	0.9046	0.0232	3.4531	12.20	0.9996
		50 mg/l	23.04	0.0493	12.79	0.9346	0.0091	5.2591	24.04	0.9995
		75 mg/l	33.84	0.0502	20.18	0.9490	0.0057	7.1672	35.46	0.9996
		100 mg/l	42.48	0.0502	41.69	0.9774	0.00185	4.1166	47.17	0.9989
	T°C	30°C	23.04	0.0493	12.79	0.9346	0.0091	5.2582	24.04	0.9995
		40°C	23.26	0.0668	13.38	0.9411	0.0151	8.6397	23.92	0.9998
		50°C	23.48	0.0576	11.35	0.9362	0.0149	8.6512	24.10	0.9999
CZA-LDH	Conc.	25 mg/l	48.08	0.0444	22.80	0.8782	0.0047	11.7647	50	0.9993
		50 mg/l	93.91	0.0426	46.53	0.8950	0.0021	20.5761	98.04	0.9995
		75 mg/l	136.59	0.0567	89.33	0.9484	0.0015	31.2500	142.86	0.9996
		100 mg/l	172.55	0.0449	133.20	0.9401	0.0006	21.3220	185.19	0.9980
	T°C	30°C	93.91	0.0426	46.53	0.895	0.0021	20.5761	98.04	0.9995
		40°C	95.65	0.0668	13.38	0.9411	0.0028	27.6243	99.01	0.9998
		50°C	96.52	0.0470	42.45	0.8821	0.0030	29.3255	99.01	0.9998

monolayer adsorption capacity and energy of adsorption (L/mg), respectively. R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. From the data calculated in Table 2, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favourable. From this research work, plot of C_e/q_e against C_e gave a straight line with slope $1/Q_0$ and intercept with b as shown in Fig. 7.

The results of Langmuir plots for both adsorbent are given in Table 2, and the maximum monolayer coverage capacity (Q_0) and Langmuir isotherm constant (b) from Langmuir isotherm model found to be 114.94 mg/g and 0.0040 L/mg, and 454.55 mg/g and 0.0042 L/mg at 30°C for ZAC-LDH and CZA-LDH, respectively. The R_L (the separation factor) calculated for both the adsorbent ZAC-LDH and CZA-LDH lies between 0 and 1 indicating that the adsorption equilibrium

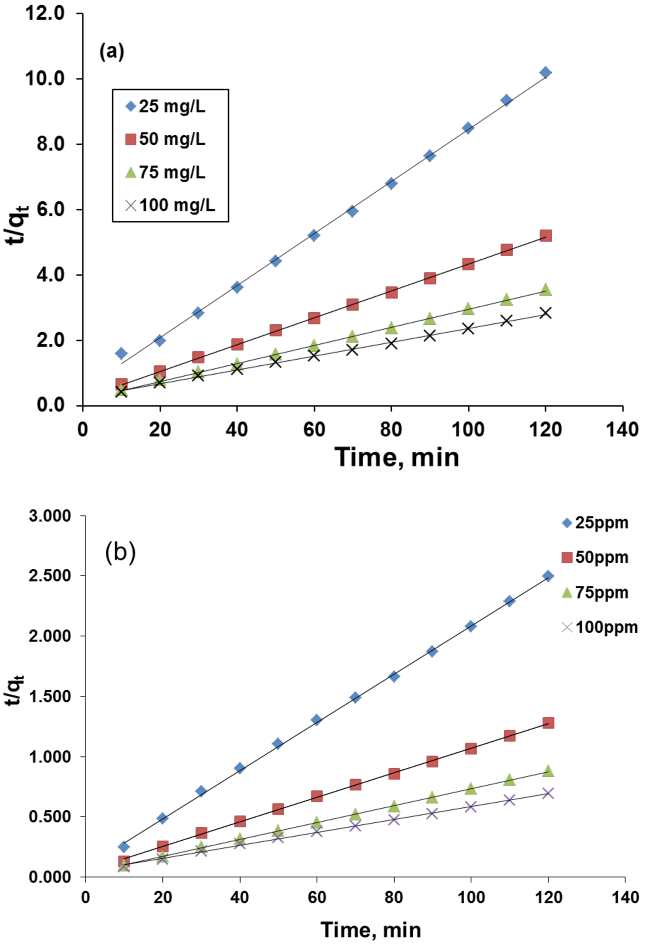

Fig. 6. Pseudo-second-order kinetic model for adsorption of AV-17 by: (a) ZAC-LDH and (b) CZA-LDH.

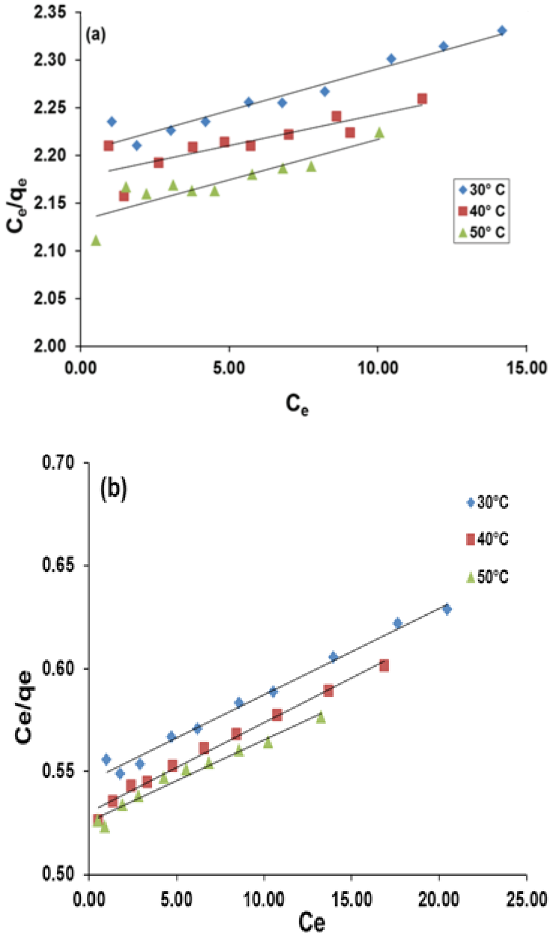

Fig. 7. Langmuir isotherms for adsorption of AV-17 by: (a) ZAC-LDH and (b) CZA-LDH.

Table 2
Isotherm parameters for adsorption of AV-17 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	114.94	0.0040	0.8333	0.9414	1.2878	5.713	0.9952
	40	151.52	0.0030	0.8696	0.7097	1.2594	6.587	0.9943
	50	117.65	0.0040	0.8333	0.7956	1.2285	7.483	0.9905
CZA-LDH	30	454.55	0.0042	0.8264	0.7389	1.246	36.008	0.988
	40	227.27	0.0086	0.6993	0.8551	1.648	63.724	0.9803
	50	217.39	0.0091	0.6873	0.9213	1.855	76.348	0.9595

process is favourable. At the same time, it does not provide satisfactory fit for Langmuir adsorption because of its lower value of correlation coefficient (R^2).

3.6.2. Freundlich model

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor 1/n. Hence, linearized form of Freundlich equation can be written as follows:

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \qquad (5)$$

where k_f is the measure of adsorption capacity n is the adsorption intensity and are calculated from intercept and slope of a linear plot of logq_e vs. logC_e (Fig. 8).

The value of n is greater than one for adsorption of AV-17 dye onto ZAC-LDH and CZA-LDH was indicating that the adsorption of AV-17 by both the adsorbent material was favourable. More over equilibrium data fitted the Freundlich isotherm with high correlation coefficient value (R^2). The much higher correlation coefficients value for the Freundlich isotherm predicts heterogeneity and multilayer adsorption of AV-17 onto both ZAC-LDH and CZA-LDH.

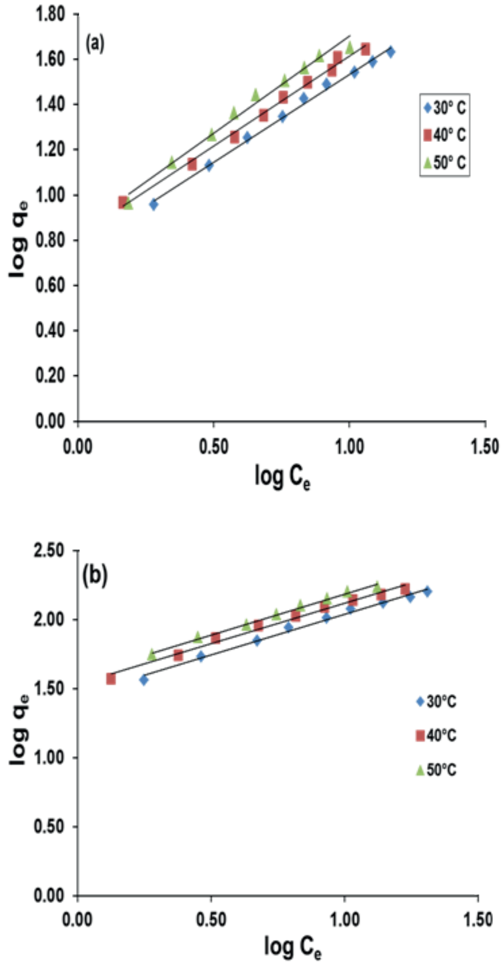

Fig. 8. Freundlich isotherm for adsorption of AV-17 by: (a) ZAC-LDH and (b) CZA-LDH.

3.7. Adsorption thermodynamics

Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy changes ($\Delta S°$) of adsorption are calculated from the binding constant, which is obtained from Langmuir equation using the following relations:

$$\Delta G^{\circ} = -RT\ln K_c \qquad (6)$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (7)$$

The $\Delta H°$ values are calculated from the slopes of linear variation of ln$K$ vs. 1/T. The negative value of $\Delta G°$ indicates the high affinity of dye to the surface of ZAC-LDH and CZA-LDH; the adsorption is favourable and spontaneous in nature. The enthalpy value $\Delta H°$ is used to distinguish between chemical and physical adsorption [54,55]. The enthalpy value $\Delta H°$ calculated for both the adsorbent ZAC-LDH (11 KJ/mol) and CZA-LDH (24 KJ/mol) is below 80 KJ/mol, and it reveals that the adsorption is physisorption [56]. Also, the positive value of $\Delta H°$ for both the adsorbents ZAC-LDH (57 KJ/mol) and CZA-LDH (102 KJ/mol) establishes that the adsorption process is endothermic. The positive $\Delta S°$ values calculated reveals the spontaneous nature of adsorption process.

3.8. Regeneration 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. The regenerated material was used for the removal of AV-17 dye from aqueous solution with the same adsorbent dosage (2 g/L for ZAC-LDH and 0.5 g/L for CZA-LDH) for 50 mg/L initial dye concentration. Four regeneration cycles were performed by thermal treatment to understand the efficiency and reusability of the materials for the AV-17 dye from aqueous solution. In the second cycle, the results showed that there was 1% and 10% increase in colour removal of dye by CZA-LDH and ZAC-LDH, respectively. In the third cycle, the dye removal was found to be decreased to 86.84% for CZA-LDH and 92.11% for ZAC-LDH, and percentage removal was less on comparison with first cycle removal efficiency of 96.97% and 87.88% by CZA-LDH and ZAC-LDH, respectively.

4. Conclusions

This study substantiates that the preparation of ZAC-LDH via co-precipitation followed by hydrothermal method at 120°C using CTAB as a soft template and its calcined product CZA-LDH and its suitability as an adsorbents for the removal of AV-17. The pseudo-second-order kinetic model describes the kinetics of AV-17 adsorption by both ZAC-LDH and CZA-LDH with high correlation coefficient following when compared with pseudo-first-order model. The equilibrium data is examined using the Langmuir and

Freundlich isotherm models. The optimum pH for the maximum adsorption of AV-17 dye was found to be 96.9% for ZAC-LDH and 99.06% for CZA-LDH at acidic pH = 3. The maximum adsorption capacities for the removal of AV-17 onto ZAC-LDH and CZA-LDH are found to be 114.94 and 454.55 mg/g at 30°C, respectively. The results prove that the synthesized CZA-LDH is more efficient than the ZAC-LDH. Moreover, the XRD pattern of CZA-LDH before and after the adsorption emphasized that the dye adsorption has significantly enhanced by reconstruction of its original layered structure by the intercalation of AV-17 dye molecule with memory effect. The pseudo-second-order kinetic model exhibited best fit while the isotherm data is well described heterogeneity and multilayer adsorption by Freundlich model. The negative value of $\Delta G°$ and positive value of $\Delta H°$ indicate that the adsorption process is spontaneous and endothermic in nature. The calculated Langmuir dimensionless separation factors R_L and n values of the Freundlich equation supports the favourability of the adsorption process. Thermal regeneration and reusability of ZAC-LDH and CZA-LDH up to three cycles are remarkable for the removal of AV-17 dye. This implies that it can be recycled and reused. These results emphasize that highly crystalline ZAC-LDH is synthesized by co-precipitation followed by hydrothermal process using CTAB, a cationic surfactant as a soft template and also its calcined product CZA-LDH found to be a suitable adsorbent for AV-17 dye from aqueous solution.

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References

[1] C. Wang, A. Yediler, D. Lienert, Z. Wang, A. Kettrup, Toxicity evaluation of reactive dyestuffs, auxiliaries and selected effluents in textile finishing industry to luminescent bacteria Vibrio fischeri, Chemosphere, 46 (2002) 339–344.

[2] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol., 97 (2006) 1061–1085.

[3] E. Rinde, W. Troll, Metabolic reduction of benzidine azo dyes to benzidine in the rhesus monkey, J. Natl. Cancer Inst., 55 (1975) 181–182.

[4] E. Bulut, M. Özacar, I.A. Şengil, Equilibrium and kinetic data and process design for adsorption of Congo Red onto bentonite, J. Hazard. Mater., 154 (2008) 613–622.

[5] P. Pandit, S. Basu, Removal of organic dyes from water by liquid–liquid extraction using reverse micelles, J. Colloid Interface Sci., 245 (2002) 208–214.

[6] M. Khadhraoui, H. Trabelsi, M. Ksibi, S. Bouguerra, B. Elleuch, Discoloration and detoxicification of a Congo red dye solution by means of ozone treatment for a possible water reuse, J. Hazard. Mater., 161 (2009) 974–981.

[7] N. Jagtap, V. Ramaswamy, Oxidation of aniline over titania pillared montmorillonite clays, Appl. Clay Sci., 33 (2006) 89–98.

[8] M.N. Chong, B. Jin, C.W. Chow, C.P. Saint, A new approach to optimise an annular slurry photoreactor system for the degradation of Congo Red: statistical analysis and modeling, Chem. Eng. J., 152 (2009) 158–166.

[9] H.Y. Zhu, R. Jiang, Y.Q. Fu, J.H. Jiang, L. Xiao, G.M. Zeng, Preparation, characterization and dye adsorption properties of γ-Fe_2O_3/SiO_2/chitosan composite, Appl. Surf. Sci., 258 (2011) 1337–1344.

[10] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater., 92 (2002) 263–274.

[11] A. Mittal, A. Malviya, D. Kaur, J. Mittal, L. Kurup, Studies on the adsorption kinetics and isotherms for the removal and recovery of Methyl Orange from wastewaters using waste materials, J. Hazard. Mater., 148 (2007) 229–240.

[12] K.V. Kumar, Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, Dyes Pigm., 74 (2007) 595–597.

[13] M. Husseien, A.A. Amer, A. El-Maghraby, N.A. Taha, Utilization of barley straw as a source of a activated carbon for removal of methylene blue from aqueous solution, J. Appl. Sci. Res., 3 (2007) 1352–1358.

[14] N. Pramanpol, N. Nitayapat, Adsorption of reactive dye by eggshell and its membrane, Kasetsart J. (Nat. Sci.), 40 (2006) 192–197.

[15] D.N. Jadhav, A.K. Vanjara, Adsorption kinetics study: removal of dyestuff effluent using sawdust, polymerized sawdust and sawdust carbon-II, Indian J. Chem. Technol., 11 (2004) 42–50.

[16] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol., 97 (2006) 104–109.

[17] P.B. Nagarnaik, A.G. Bhole, G.S. Natarajan, Adsorption of arsenic on flyash, Indian J. Environ. Health, 45 (2003) 1–4.

[18] B.P. Kelleher, M.N. O'Callaghan, M.J. Leahy, T.F. O'Dwyer, J.J. Leahy, The use of fly ash from the combustion of poultry litter for the adsorption of chromium(III) from aqueous solution, J. Chem. Technol. Biotechnol., 77 (2002) 1212–1218.

[19] M. Mahadeva Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Sorption characteristics of O-cresol on bagasse fly ash and activated carbon, Indian J. Environ. Health, 40 (1998) 67–78.

[20] Y.C. Sharma, Adsorption of Cr (IV) onto Wollastonite: effect of pH, Indian J. Chem. Technol., 8 (2001) 186–190.

[21] K. Kadirvelu, C. Namasivayam, Agricultural by-product as metal adsorbent: sorption of lead(II) from aqueous solution onto coirpith carbon, Environ. Technol., 21 (2000) 1091–1097.

[22] K. Manjula Rani, P.N. Palanisamy, S. Gayathri, S. Tamilselvi, Adsorptive removal of basic Violet dye form aqueous solution by activated carbon prepared form tea dust material, Int. J. Innov. Res. Sci. Eng. Technol., 4 (2015) 6845–6853.

[23] S. Sadaf, H.N. Bhatti, S. Nausheen, M. Amin, Application of a novel lignocellulosic biomaterial for the removal of Direct Yellow 50 dye from aqueous solution: batch and column study, J. Taiwan Inst. Chem. Eng., 47 (2015) 160–170.

[24] S. Sadaf, H.N. Bhatti, S. Nausheen, S. Noreen, Potential use of low-cost lignocellulosic waste for the removal of direct violet 51 from aqueous solution: equilibrium and breakthrough studies, Arch. Environ. Contam. Toxicol., 66 (2014) 557–571.

[25] S. Sadaf, H.N. Bhatti, Response surface methodology approach for optimization of adsorption process for the removal of Indosol Yellow BG dye from aqueous solution by agricultural waste, Desal. Wat. Treat., 57 (2016) 11773–11781.

[26] S. Sadaf, H.N. Bhatti, Batch and fixed bed column studies for the removal of Indosol Yellow BG dye by peanut husk, J. Taiwan Inst. Chem. Eng., 45 (2014) 541–553.

[27] A. Mittal, L. Kurup, Column operations for the removal and recovery of hazardous dye 'Acid Red-27' from aqueous solutions, using waste materials-bottom ash and de-oiled soya, Ecol. Environ. Conserv., 12 (2006) 181–186.

[28] A. Mittal, M. Naushad, G. Sharma, Z.A. Alothman, S.M. Wabaidur, M. Alam, Fabrication of MWCNTs/ThO_2 nanocomposite and its adsorption behavior for the removal of Pb(II) metal from aqueous medium, Desal. Wat. Treat., 57 (2016) 21863–21869.

[29] A. Mittal, R. Ahmad, I. Hasan, Biosorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions from aqueous solutions by L-cystein-modified montmorillonite-immobilized alginate nanocomposite, Desal. Wat. Treat., 57 (2016) 17790–17807.

[30] A. Mittal, R. Ahmad, I. Hasan, Iron oxide-impregnated dextrin nanocomposite: synthesis and its application for the biosorption of Cr(VI) ions from aqueous solution, Desal. Wat. Treat., 57 (2016) 15133–15145.

[31] A. Mittal, R. Ahmad, I. Hasan, Poly(methyl methacrylate)-grafted alginate/Fe_3O_4 nanocomposite: synthesis and its application for the removal of heavy metal ions, Desal. Wat. Treat., 57 (2016) 19820–19833.

[32] G. Sharma, M. Naushad, D. Pathania, A. Mittal, Modification of *Hibiscus cannabinus* fiber by graft copolymerization: application for dye removal, Desal. Wat. Treat., 54 (2015) 3114–3121.

[33] A. Mittal, J. Mittal, Hen Feather: A Remarkable Adsorbent for Dye Removal, Green Chemistry for Dyes Removal from Wastewater: Research Trends and Applications, Scrivener Publication LLC, USA, 2015, pp. 409–457.

[34] J.S. Valente, F. Tzompantzi, J. Prince, J.G. Cortez, R. Gomez, Adsorption and photocatalytic degradation of phenol and 2,4-dichlorophenoxiacetic acid by Mg–Zn–Al layered double hydroxides, Appl. Catal., B, 90 (2009) 330–338.

[35] E. Dvininov, M. Ignat, P. Barvinschi, M.A. Smithers, E. Popovici, New SnO_2/MgAl-layered double hydroxide composites as photocatalysts for cationic dyes bleaching, J. Hazard. Mater., 177 (2010) 150–158.

[36] Z.M. Ni, S.J. Xia, L.G. Wang, F.F. Xing, G.X. Pan, Treatment of methyl orange by calcined layered double hydroxides in aqueous solution: adsorption property and kinetic studies, J. Colloid Interface Sci., 316 (2007) 284–291.

[37] C. Nethravathi, J.T. Rajamathi, N. Ravishankar, C. Shivakumara, M. Rajamathi, Graphite oxide-intercalated anionic clay and its decomposition to graphene − inorganic material nanocomposites, Langmuir, 24 (2008) 8240–8244.

[38] Y. Zhao, M. Wei, J. Lu, Z.L. Wang, X. Duan, Biotemplated hierarchical nanostructure of layered double hydroxides with improved photocatalysis performance, ACS Nano, 3 (2009) 4009–4016.

[39] S.J. Palmer, R.L. Frost, Use of hydrotalcites for the removal of toxic anions from aqueous solutions, Ind. Eng. Chem. Res., 49 (2010) 8969–8976.

[40] S.V. Prasanna, P.V. Kamath, Chromate uptake characteristics of the pristine layered double hydroxides of Mg with Al, Solid State Sci., 10 (2008) 260–266.

[41] D.G. Evans, X. Duan, Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine, Chem. Commun., 5 (2006) 485–496.

[42] Y. Yasin, A.H. Abdul Malek, S. Mariam Sumari, Adsorption of eriochrome black dye from aqueous solution onto anionic layered double hydroxides, Orient. J. Chem., 26 (2010) 1293–1298.

[43] S. Miyata, The syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties. I: The systems Mg^{2+}-Al^{3+}-NO^{3-}, Mg^{2+}-Al^{3+}-Cl^-, Mg^{2+}-Al^{3+}-Cl O_4^-, Ni^{2+}-Al^{3+}-Cl^- and Zn^{2+}-Al^{3+}-Cl, Clay Clay Miner., 23 (1975) 369–375.

[44] Z.P. Xu, G.Q. Lu, Hydrothermal synthesis of layered double hydroxides (LDHs) from mixed MgO and Al_2O_3: LDH formation mechanism, Chem. Mater., 17 (2005) 1055–1062.

[45] D. Carriazo, M. Del Arco, E. Garcia-Lopez, G. Marci, C. Martin, L. Palmisano, V. Rives, Zn, Al hydrotalcites calcined at different temperatures: preparation, characterization and photocatalytic activity in gas–solid regime, J. Mol. Catal. A: Chem., 342 (2011) 83–90.

[46] F.L. Theiss, M.J. Sear-Hall, S.J. Palmer, R.L. Frost, Zinc aluminium layered double hydroxides for the removal of iodine and iodide from aqueous solutions, Desal. Wat. Treat., 39 (2012) 166–175.

[47] F.P. de Sá, B.N. Cunha, L.M. Nunes, Effect of pH on the adsorption of Sunset Yellow FCF food dye into a layered double hydroxide (CaAl-LDH-NO_3), Chem. Eng. J., 215 (2013) 122–127.

[48] B. Acemioğlu, Adsorption of Congo red from aqueous solution onto calcium-rich fly ash, J. Colloid Interface Sci., 274 (2004) 371–379.

[49] Y.C. Sharma, V. Srivastava, C.H. Weng, S.N. Upadhyay, Removal of Cr(VI) from wastewater by adsorption on iron nanoparticles, Can. J. Chem. Eng., 87 (2009) 921–929.

[50] I. Chaari, E. Fakhfakh, S. Chakroun, J. Bouzid, N. Boujelben, M. Feki, F. Jamoussi, Lead removal from aqueous solutions by Tunisian smectitic clay, J. Hazard. Mater., 156 (2008) 545–551.

[51] S. Lagergren, About the theory of so-called adsorption of soluble substances , K. Sven. Vetenskapsakad. Handl., 24 (1898) 1–39.

[52] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[53] L. Wang, A. Wang, Adsorption properties of Congo Red from aqueous solution onto surfactant-modified montmorillonite, J. Hazard. Mater., 160 (2008) 173–180.

[54] J. Budhraja, M. Singh, Spectrophotometric study of adsorption of bromo thymol blue on charcoal and phosphates of FeIII, AlIII, CrIII and ZnII, J. Indian Chem. Soc., 81 (2004) 573–575.

[55] M. Doula, A. Ioannou, A. Dimirkou, Thermodynamics of copper adsorption-desorption by Ca-Kaolinite, Adsorption, 6 (2000) 325–335.

[56] V. Gopal, K.P. Elango, Studies on defluoridation of water using magnesium titanate, Indian J. Chem. Technol., 17 (2010) 28–33.