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LAYERED DOUBLE HYDROXIDES AS ADSORBENTS FOR ANIONIC DYE REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract

Reactive Blue 19 (RB 19) dye removal from aqueous solutions by using layered double hydroxides containing nitrate as the intergallery anion (MgAlLDH) as adsorbents was investigated. The adsorption process was found to be influenced by the contact time, the initial dye concentration, the presence of inorganic anions and the temperature. The XRD and FTIR analysis evidence two competitive processes: adsorption and/or intercalation of the molecules may take place, depending on the initial dye concentration. The equilibrium dye adsorption increased from 62 to 350 mg/g as the initial RB 19 concentration was risen from 0.5 to 3.0 mg/mL. The adsorption capacity decreases in the presence of electrolytes. The experimental data are well fitted with the Langmuir isotherm equation. The thermodynamic parameters were calculated. The resulting negative ΔS° value correlated with a positive value of ΔH° indicate that the adsorption process is spontaneous and endothermic. In addition, the regeneration of MgAlLDH after RB 19 adsorption was also investigated and proved feasible only in the first cycle.

Key words: adsorption, layered double hydroxide, reactive blue 19, thermodynamic constants

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1. Introduction

Environmental pollution reduction by implementing ecological technologies is currently a high priority for the scientific community. Large quantities of dyes are annually produced and used in textile, cosmetics, paper, leather, pharmaceutical, food and other industries. Approximately 15% of the dye produced globally is lost during the dyeing process and discharged in the textile effluents (El Gaini et al., 2009).

The presence of dyes in wastewater poses severe problems to the environment, due to their synthetic nature, poor degradability and difficulty to treat by conventional methods. Dyes are stable to light and heat, and some are proven to be toxic to microorganisms, having a negative impact upon photosynthetic activity in aquatic systems (Sumari et al., 2009). Treatments aimed to eliminate dyes from textile wastewater are prioritized and regulated by government legislation since even small amounts are highly visible and toxic (Salleh et al., 2011).

Many researchers have studied various techniques in order to remove the dyes from wastewaters, for example, the use of coagulant/flocculant agents, advanced processes of oxidation, ozonation, nanofiltration and adsorption on various supports such as solid agriculture waste, gallinaceous feathers (Figueiredo and Freitas, 2013), pumice stone (Samarghandi et al., 2013), different types of activated carbon, montmorillonite impregnated with tensioactive agents, etc. (Itoh et al., 2005). Due to low biodegradability, a conventional biological treatment is not considered efficient, while the adsorption on activated carbon has proven to be an effective process, with the disadvantage of high cost (Purkait et al., 2004). However, among all these methods, the adsorption has been preferred due to the

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high quality of the treated effluents, especially for well-designed sorption processes (Javadian et al., 2014). Low-cost materials, in their natural and modified forms, have been also extensively studied as alternative adsorbents for dyes (Ahmad et al., 2007; Gurses et al., 2006). Among the various adsorbents, layered double hydroxides (LDHs) are promising waste scavengers, particularly for dye molecules (Allmann, 1968).

Recent studies showed that the use of LDHs for the retention of organic anions has shown very good results (De Roy et al., 1992; Lakraimi et al., 2000; Silion et al., 2013). Adsorption of dyes by LDHs is a facile method for cleaning up effluents and wastewater before discharging them into the environment (Abdelkader et al., 2011; Ahmed and Gasser, 2012; Auxilio et al., 2009; Bouhent et al., 2011; Dos Santos et al., 2013; Elkhattabi et al., 2013; Extremera et al., 2012; Guo et al., 2013; Malek and Yasin, 2012; Monash and Pugazhenthi, 2014; Pereira de Sa et al., 2013).

LDHs, also known as anionic clays, are materials of great interest due to their hydrophobic nature and large specific surface area, high anionic exchange capacity and good adsorption ability. The layered structure of the LDHs creates the premises for intercalating large organic or inorganic anions such as dyes, drugs, pesticides, enzymes, polymers, etc. generating hybrid inorganic-organic nanostructures (Chun et al., 2009; De Roy, 1998; Hosni et al., 2009; Nalawade et al., 2009). LDHs are characterised by a lamellar structure similar to that of the brucite Mg $(OH)_2$ in which the Mg^{2+} ions are replaced by trivalent ions like M^{3+}_x. 3.

The general formula describing these materials is: $[M^{II}_{1-x}M^{III}_x\ (OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where: M^{II} and M^{III} are divalent and trivalent cations respectively, A^{n-} is the compensation anion and x is the molar fraction of the trivalent cation ($M^{III}/[M^{II} + M^{III}]$). A large number of divalent and trivalent metals are able to combine to form LDHs layers (Cavani et al., 1991).

The aim of the present work is to assess the adsorption capacity of MgAlLDH for the RB 19 dye and to understand the mechanism involved. The influences of contact time, initial dye concentration, amount of LDHs, the temperature and the inorganic anion competition upon the adsorption process have been studied. The localization of the dye in the interlayer space and/or on external surfaces of the LDHs is studied by XRD and FTIR analyses.

2. Materials and methods

2.1. Materials

All chemicals, including Mg $(NO_3)_2 \times 6H_2O$, $Al(NO_3)_3 \times 9H_2O$ and Reactive Blue 19 (RB 19), were purchased from Sigma-Aldrich and were used without further purification. Deionized water was used for the preparation of all aqueous solutions. The chemical structure of the dye is shown in Fig. 1.

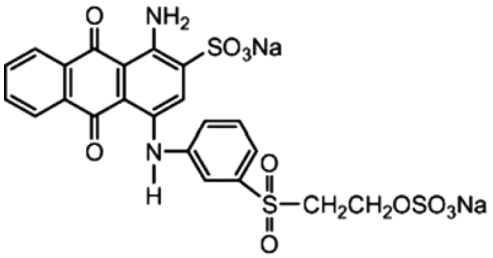

Fig. 1. Structural formula of Reactive Blue 19

2.2. Synthesis of MgAlLDH

The MgAlLDH was synthesized by co-precipitation method at a constant pH value of 9.7 and a temperature of 60°C (according to the method described by Miyata, 1980). 100 ml aqueous solution containing 0.1 mol of $Mg(NO_3)_2 \times 6H_2O$ and 0.05 mol of $Al(NO_3)_3 \times 9H_2O$ (Mg/Al = 2) was delivered with 0.4 ml/min flow rate into a round bottom flask containing 60 ml deionized water that was previously bubbled with nitrogen for half an hour in order to remove carbonate anion contamination. The pH was maintained constant by simultaneous addition of a 1.0 N NaOH solution, using a TitraLab TIM 854 apparatus. The resulting white precipitate was aged at room temperature for 18 h under stirring and then for 30 h without stirring. After the ageing step, the precipitate was separated by centrifugation, washed extensively several times with deionized water until reaching a pH value of 7, then dried overnight under vacuum at 70°C.

2.3. Characterization techniques

X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D8 diffractometer using monochromatic CuK α radiation (λ =0.154 nm), operating at 40 kV and 50 mA over a 2θ range from 4 to 70 degree. FTIR spectra were recorded on a FT-IR Bomem MB 104 spectrometer under the following experimental conditions: 200 scans in the mid-IR range (400-4000 cm^{-1}) using KBr (ratio 5 / 95 wt %) pellets, and a resolution of 4.0 cm^{-1}.

2.4. Adsorption experiments

The adsorption experiments were carried out using the batch equilibrium technique at different temperatures in the range of 15°C-45°C, at pH= 6.8 and under a stream of N_2. 0.4 g of MgAlLDH were dispersed in 50 mL of RB 19 solutions. The initial dye concentration was varied between 0.5 and 3 mg/mL. The solution has been washed, filtrated and the solid products obtained have been dried under vacuum at 100°C for 3 hours and used for analysis. The concentration of textile dye RB 19 was determined by the spectrophotometric method. Samples were taken at certain periods of time.

The absorbance for each sample was measured at 594 nm on a Nanodrop 1000 Spectrophotometer. The amount of RB 19 adsorbed by MgAlLDH, *Q*, was calculated as the difference between initial and equilibrium (final) concentrations of the dye in solution (C_i and C_t, respectively) by a given mass of the adsorbent (m) in the volume of solution, V (Elkhattabi et al., 2013)(Eq. 1):

$$Q = \frac{(Ci - Ct) \times V}{m} \tag{1}$$

3. Results and discussion

3.1. Powder X-ray diffraction

The XRD patterns recorded for the MgAlLDH matrix, the corresponding hybrid materials MgAlLDH-RB 19, the calcined MgAlLDH-RB 19 (CMgAlLDH) after the adsorption and for the reconstruction material are presented in Fig. 2. The diffractogram of the original LDH (Fig. 2a) has a typical layered structure similar to those reported in the literature for these materials (Xu and Zeng, 2001). The diffraction peak found at 8.79 Å on the MgAlLDH diffractogram corresponds to the basal spacing of LDHs with nitrate anions in the interlayer (Myata, 1983).

The diffratogram recorded for MgAlLDH-RB 19 after adsorption in the dye concentration range located below 0.5 mg/mL (Fig. 2b), the cristallinity of the sample is a bit diminished compared with that shown by the original LDH, as indicated by the decrease in the distance of the basal space (d_{003}), that was reduced from 8.79 Å to 8.41 Å (Elkhattabi et al., 2013). At higher dye concentration (more than1.5 mg/mL), both the adsorption process and the intercalation of anionic molecule of the dye into the LDH structure took place. The intercalation of the dye anions cause an increase in the interlayer space from d_{003} = 8.79 Å to d_{003} = 9.59 Å This diffractogram feature is in good agreement with values reported by other authors (Elkhattabi et al., 2013; Rubino, 2001) and it is explained by the exchange of the nitrate anion with the RB 19 anions (Fig. 2c).

The XRD pattern recorded for the CLDH (Fig. 2d) indicated that the layered double hydroxides structure is destroyed and evidenced only the presence of MgO (Crepaldi et al., 2002; Thomas et al., 2006; You et al., 2002). This observation might suggest an almost total decomposition of the MgAlLDH and elimination of most interlayer nitrate anions and water. After the dye adsorption onto CLDH, the layered double structure has been mostly reconstructed (Fig. 2e). It was also observed that the intensity of the peaks decreased compared with the original LDH, suggesting a lowered cristallinity due to the calcination and regeneration processes. The basal space of the material after the last cycle of reconstruction was d_{003}= 8.07 Å.

3.2. FTIR spectroscopy

The FTIR spectra of the MgAlLDH and MgAlLDH-RB 19 samples are presented in Fig. 3.

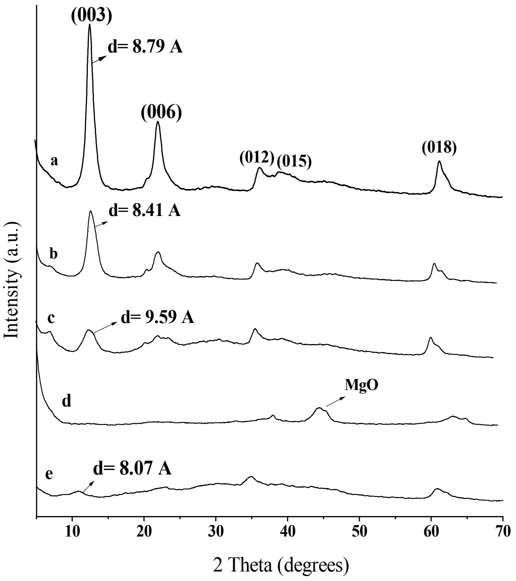

Fig. 2. Powder XRD patterns for MgAlLDH (a), MgAlLDH-RB19, 0.5 mg/mL (b), MgAlLDH-RB19, 3 mg/mL (c), CLDH (d), CLDH after RB 19 adsorption (e)

The broad and strong band in the frequency range of 3600-3200 cm^{-1}, centered at 3466 cm^{-1}, is common for all the hydrotalcite type materials corresponding to the OH stretching vibration due to the presence of water molecules (De Roy et al., 2001). The bands observed in the low-frequency region of the spectrum are associated with the lattice vibration modes in the LDH sheets and may be assigned to the M-O bond in the wavenumber range of 781 to 675 cm^{-1} and respectively to the M-O-M bond located near 447 cm^{-1} (M = Al, Mg) (Cavani et al., 1991). The appearance of a strong band at 1384 cm^{-1} is due to the symmetric vibration of the interlayer nitrate anion belonging to the MgAlLDH (Silion et al., 2010). All the vibration bands associated with the organic anion, as well as the adsorption bands characteristic for LDHs are evidenced in the spectra recorded for MgAlLDH-RB 19 sample (Fig. 3b, c).

The asymmetric stretching vibration related to the S=O bond appears in the 1273-1155 cm^{-1} region. The adsorption bands at 1674 and 1474 cm^{-1} are assigned to the stretching vibration of the C=C bond belonging to an aromatic ring, while the bands at 1634 and 1182 cm^{-1} are assigned to those of C=O and respectively C-N bond (Elkhattabi et al., 2013). The absence of the 1384 cm^{-1} band from the spectrum of the MgAlLDH-RB 19 (Fig. 3c) sample obtained when the initial RB 19 concentration is higer than 1.5 mg/mL, confirms the fact that the interlayer nitrate anions have been displaced (Silion et al., 2012). For the MgAlLDH-RB 19 sample obtained when using an initial dye concentration that is lower than 1.5 mg/mL, the band characteristic to the nitrate anion is evidenced (Fig. 3b). In this case, only the adsorption of the dye occurs. The FTIR analysis correlated with the XRD reveal that the interaction between the matrix and the dye is, depending on the initial concentration of the latter, a competitive process comprising two sides: adsorption and intercalation.

3.3. Adsorption equilibrium

3.3.1. Effect of contact time and initial dye concentration

The dye concentration is an important parameter characterizing the mass transfer of the anionic molecules between the aqueous and solid phase. The effect of initial RB 19 concentration upon the adsorption efficiency was evaluated in the concentration range of 0.5 to 3.0 mg/mL, while the temperature and LDH amount were kept at 25° C and 0.4 g, respectively. The results are presented in Fig. 4**.** The equilibrium adsorption capacity increased with increasing the initial dye concentration, due to the increase in the amount of anions competing for the available binding sites on the LDH surface.

The equilibrium amount of adsorbed dye increased from 62 to 350 mg/g as the initial RB 19 concentration increased from 0.5 to 3.0 mg/mL. The results show that dye uptake is rapid in the first stage, lasting about 60 minutes, and then changes slowly towards saturation, attained after 240 minutes. The time required for reaching equilibrium increases at higher initial dye concentrations.

3.3.2. Effect of inorganic anion competition

Textile industries generally use large amounts of salts in the fabric dyeing process (Baocheng et al., 2008, Netpradit et al., 2004). Typical formulations involve Na_2SO_4 (50 g/L) and Na_2CO_3 (5g/L) solutions when RB 19 is the dye of choice.

It is therefore important to investigate the effect of these anions upon the dye removal efficiency when MgAlLDH is used as and adsorbent. The following procedure was used: 5g Na_2SO_4 , 0.5 g Na_2CO_3 and 50 mg MgAlLDH were added to 100 mL RB 19 solution with a concentration of 0.15 mg/mL (the parameters are almost similar to the composition of the wastewater from textile industry). Effect of coexisting ions upon the dye adsorption of the MgAlLDH is shown in Fig. 5.

The decreased adsorption efficiency in the presence of the electrolytes is due to the interaction between the surface and the added solutes that may block some of the sorption active sites otherwise available for the dye molecules, and probably to the competitive process of intercalation of the inorganic and organic anions of the dye.

The dye uptake was reduced when the dye solution contained Na_2SO_4 and Na_2CO_3, compared to the case where no electrolyte was added. The adsorption efficiency of the dye in the absence of the electrolytes is determined after 420 minutes and it is 71.25 %, while in the presence of SO_4^{2-} anions, the removal efficiency is 58.75 % and it is reached after 480 minutes. The maximum reduction in the removal efficiency was 50 % in the presence of CO_3^{2-} ions. This result is consistent with those reported in the literature and showed that in the case in which both SO_4^{2-} and CO_3^{2-} coexist, they had a significant effect upon the adsorption of dye (Parsa and Abbasi, 2007). It has been also demonstrated that the interlayer CO_3^{2-} ions in LDHs are difficult to be exchanged by other anions (Goswamee et al., 1988; Inacio et al., 2001; Toraishi et al., 2002).

3.3.3. Effect of temperature

The adsorption process depends on the temperature and this parameter has the following effect. Increasing the temperature is known to modify the diffusion rate of the adsorbate molecule within the matrix, owing to the decrease in the solution viscosity. Also, changing the temperature will modify the equilibrium capacity of the adsorbant for a particular adsorbate (Khezami and Capart, 2005).

The effect of temperature on the removal of dye was studied by varying adsorption temperatures from 15°C to 45°C by adjusting the temperature controller on the water bath shaker, using 50 mL solution aliquots with initial dye concentrations in the range of 0.5-3 mg/mL.

Fig. 6 displays the adsorption curves obtained under various isothermal conditions. The LDH equilibrium adsorption capacity for RB 19 was higher with increasing temperature, ranging from 172 mg/g at 15°C to 321 mg/g at 25°C, to 451 mg/g at 35°C and to 548 mg/g at 45°C. This trend indicates that the dye adsorption on MgAlLDH was favored at higher temperature.

3.4. Thermodynamic study of RB 19 adsorption by MgAlLDH

The thermodynamic parameters provide information about the inherent energetic changes associated with the adsorption process.

The standard free energy (ΔG^o), standard entalphy (ΔH^o) and standard entropy (ΔS^o) were calculated using the following equations (Eqs. 2-4):

$$\Delta G^o = - RT \ln K_L \quad (2)$$

$$\Delta G^o = \Delta H^o - T \Delta S^o \quad (3)$$

$$\ln K_L = \Delta S^o / R - \Delta H^o / RT \quad (4)$$

where R (8.314 J/molK) is the universal gas constant, T (K) is the absolute solution temperature, and K_L (L/mg) is the Langmuir isotherm constant. ΔG^o can be calculated from the Langmuir model by using Eq. (3) and the value of the equilibrium constant K_L determined at each temperature. The standard entalphy (ΔH^o) and standard entropy (ΔS^o) values can be calculated from the slope and intercept of the plot of $\ln K_L$ versus $1/T$ (Eq. 5).

The values of these parameters are presented in Table 1. The positive value of $\Delta H°$ confirms the endothermic nature of the dye adsorption process. Generally speaking, a value of $\Delta H°$ between 5 and 40 kJ mol^{-1} is characteristic for a physisorption mechanism, while an enthalpy in the range of 40 to 800kJ mol^{-1} corresponds to chemisorption mechanism (Crini and Badot, 2008). The negative value of $\Delta S°$ indicates a rather good affinity of the material for the dye molecules and it is a sign of an increase in the degree of freedom of the adsorbed species, compared to their unbound state (Hu et al., 2007; Renault et al., 2008; Zhu et al., 2005).

3.5. Regeneration of MgAlLDH-RB 19

In order to reuse the adsorbent after completing equilibrium adsorption experiments, the suspensions were recovered, filtered, dried on a thermobalance (Mettler Toledo HG63 Moisture Analyzer) and calcined at 550°C again for 4 h.

The calcined materials (CMgAlLDH), in portions of 0.4 g, were re-dispersed in 50 mL of RB 19 solution with 3 mg/mL concentration. This procedure was repeated three times and the amount of RB 19 adsorbed after each dispersion-calcination cycle was determined.

The adsorption of RB 19 using MgAlLDH and CMgAlLDH after thermal treatment is shown in Fig. 7. After the first-cycle regeneration, CLDH sorption capacity decreased from 281 mg/g to 230 mg/g, a percentage decrease of 13 % compared with the original MgAlLDH. This is not in agreement with the LDH adsorption behavior as reported by Zhu et al. (2005). These authors observed that the Brilliant Blue adsorption capacity decreased about 69 % compared with the original calcined LDH after the first regeneration cycle. In the following regeneration cycles, the adsorption capacity decreased significantly, at 122 mg/g in the second cycles and respectively 88 mg/g in the third cycle.

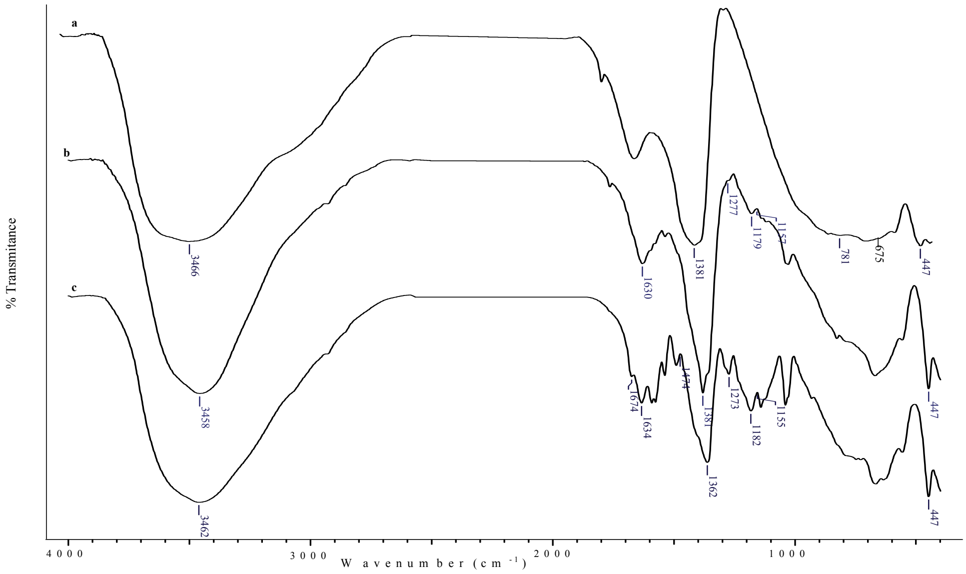

Fig. 3. FTIR spectra of MgAlLDH (a), MgAlLDH-RB 19, concentration of RB 19- 0.5 mg/mL (b), MgAlLDH-RB 19, concentration of RB 19-3 mg/mL (c)

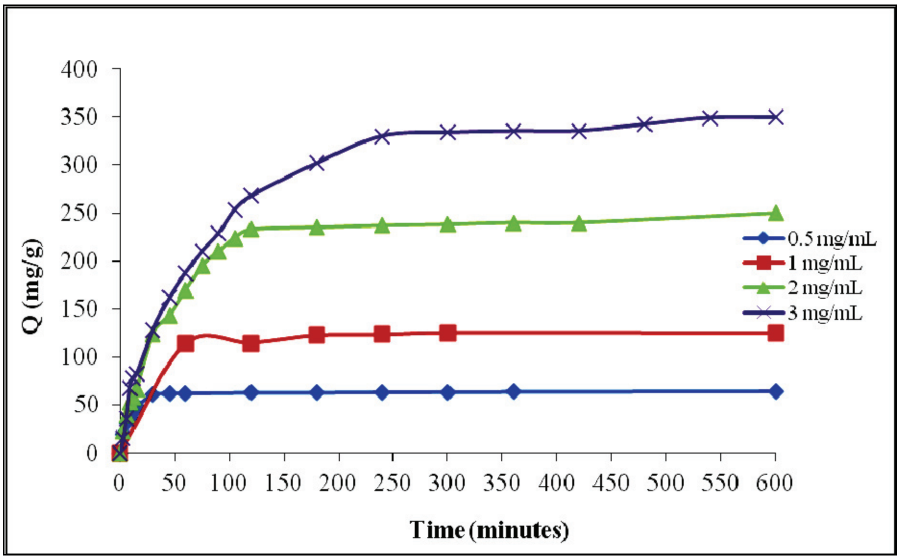

Fig. 4. Effect of contact time and initial concentration of RB 19 on the extent of adsorption

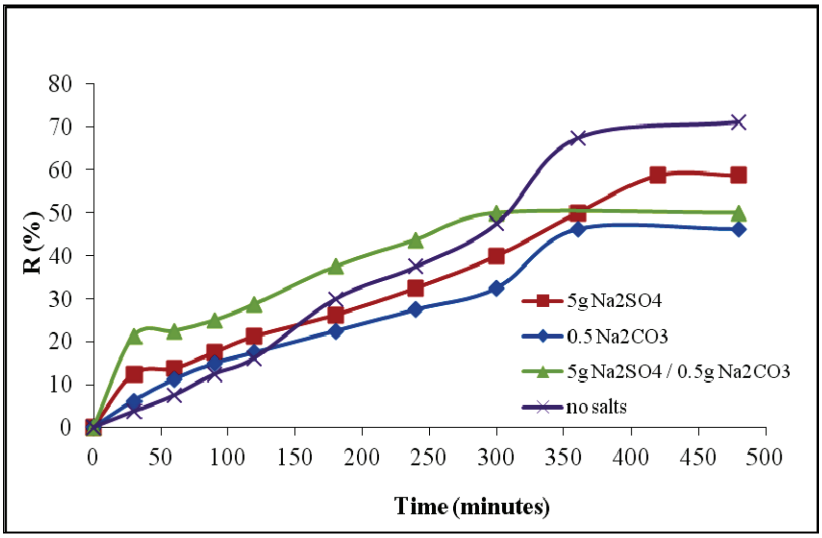

Fig. 5. Effect of co-existing anions on the removal efficiency

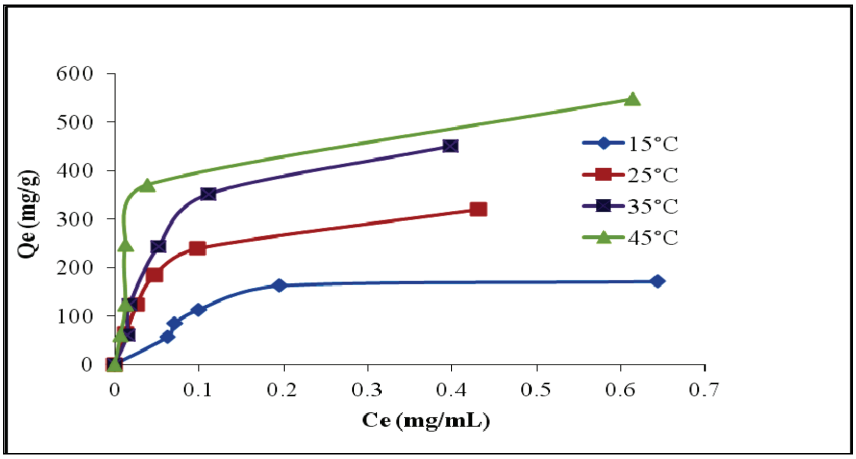

Fig. 6. The adsorption isotherms

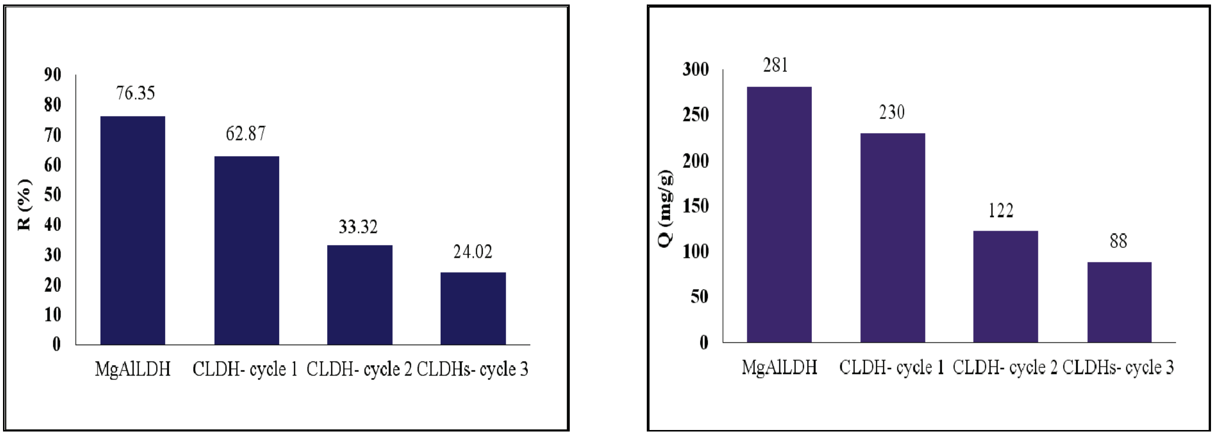

Fig. 7. Adsorption of RB 19 using MgAlLDH and CMgAlLDH

Table 1. Thermodynamic parameters for the adsorption of RB 19 on MgAlLDH

Thermodynamic constants						
MgAlLDH	*$\Delta G°$ (kJ mol^{-1})*				*$\Delta H°$ (kJ mol^{-1})*	*$\Delta S°$ (J mol^{-1} K^{-1})*
	15°C	25°C	35°C	45°C		
MgAlLDH-RB 19	- 1.955	- 4.423	- 5.585	- 6.066	37.18	-135.88

In our experiments, the results are consistent with those reported by Ni et al. (2007) in the adsorption of methyl orange on MgFeLDH. This behavior is probably due to the progressive decreasing in crystallinity of the LDH-like materials in structural reconstruction of the calcined materials, leading to lower adsorption capacity (Ni et al., 2007).

4. Conclusions

This study shows that MgAlLDH can be used as an efficient adsorbent for the removal of the RB 19 dye from solutions with compositions that mimick real textile waste-water. The mechanism of adsorption on external surfaces and intercalation by reconstruction of calcined material was confirmed by XRD and FTIR analysis.

The processing parameters such as, contact time and initial dye concentration, inorganic anion competition and temperature can affect the adsorption process. The adsorption data are fitted well with the Langmuir isotherm equation. The thermodynamic parameters were calculated and the negative ΔS ° and positive $\Delta H°$ indicate that the adsorption process is spontaneous and endothermic under the experimental conditions.

Thermal treaments for regenerating MgAlLDH after RB 19 adsorption suggest that this material can be recycled and re-used.

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