




Acid Green 1 removal from wastewater by layered double hydroxides

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Abstract

The paper presents the removal of Acid Green 1 (AG1) from aqueous solutions by [Zn–Al–Cl]-layered double hydroxides (LDHs). The LDH was prepared by coprecipitation at constant pH. The affinity of this material for AG1 was studied as a function of contact time, pH of the solution, LDH dose and AG1/LDH mass ratio. It was found that 32 h are enough to reach the equilibrium with a maximum retention at pH 8 for an LDH dose of 100 mg and with an AG1/LDH mass ratio higher than 2. The adsorption isotherm is of L-type, as described by the Langmuir model. The results demonstrate that AG1 retention on LDHs occurs by adsorption on external surface when AG1/LDH mass ratio is equal or lower than 2 and by both adsorption and interlayer ion exchange for ratios higher than 2. A mechanism for the AG1 removal has been confirmed by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric–differential thermal analyses and scanning electron microscopy.

Keywords Layered double hydroxides · Acid Green 1 · Dye · Adsorption · Anion exchange

Introduction

Freshwater resources are under threat due to activities from expanding population and increasing rate of overuse. The presence of effluents from industrial, agricultural and domestic sources is responsible for water pollution and harms the environment (Tan et al. 2007). The reduction of pollution by implementing environment-friendly technologies is currently a very high priority. Synthetic dyes are amongst these harming effluents and are used in many industries, including textile, leather tanning, printing, and food processing (Batzias and Sidiras 2007). These coloured contaminants are difficult to eliminate from water because of their high

stability, poor biodegradability and the difficulty in treating them with conventional methods.

The textile and clothing industries use large amounts of water-soluble synthetic organic dyes in their processes. These colouring agents are sometimes very stable, even when exposed to light and heat, and some were found to be toxic to microorganisms. In addition, their presence in aquatic systems reduces light penetration and thus retards photosynthesis (Sumari et al. 2009).

The global import and export market for dispersed dyes and their preparations accounted for 570,000 metric tons in 2011 (Ghaly et al. 2014). The amounts of water have been estimated at 0.08–0.15 m³ per kg of fabrics depending on the type to be produced (Moustafa 2008). Since the dyeing process is not very efficient, large concentrations of dyestuffs are discharged in textile effluents. These were estimated at 15% worldwide (El Gaini et al. 2009).

The treatment of effluents from textile industries is usually carried out by physico-chemical techniques, such as flocculation, coagulation, advanced oxidation and ozonation, and biological methods to remove organic matters, nitrogen, phosphorus and metals. The traditional biological and chemical methods have proven to be inefficient given the low biodegradable nature of most of the dyes (Tabak et al. 2009; Fu and Viraraghavan 2001). Therefore, the removal of

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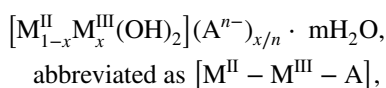
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dyes by environment-friendly and economic technologies is currently high priority for the scientific community.

Adsorption has been found to be promising due to the ease in adsorbent management and the possibility of their recycling as well as the water purification outcome. Several studies have been conducted to evaluate various natural and synthetic sorbents, among which are activated carbons and clays (Javadian et al. 2014; Forgacs et al. 2004; Aydin and Yavuz 2004; Ayad and El-Nasr 2012).

Layered double hydroxides (LDHs) have proven to be good candidates for removing anionic dyes from aqueous solutions. These materials, which are endowed with high anionic exchange capacity and good adsorptive ability, have been able to retain and host several large organic anions (Lakraimi et al. 2000; Li et al. 2005) including dyestuffs (Dos Santos et al. 2013; Elkhatabi et al. 2013; Guo et al. 2013; Pereira et al. 2013; Alexandrica et al. 2015).

LDHs, also called hydrotalcite-like compounds and anionic clays, are based on the brucite, $Mg(OH)_2$, layers with partial substitution of trivalent for divalent cations. The net positive charge is then balanced by exchangeable hydrated anions (Rives 2001). They are commonly represented by the general formula:



where M^{II} and M^{III} are divalent and trivalent cations, A^{n-} is the interlayer anion and x the $M^{II}/(M^{II} + M^{III})$ ratio.

These materials offer a large spectrum of application opportunities because of their stability and their anion exchange properties, allowing for their intercalation and desintercalation. The importance of LDH compounds led to a very rich literature and several books and review articles have been devoted to their structure, properties and applications (Rives 2001; Evans and Slade 2006; Braterman et al. 2004; Duan and Evans 2006).

Metal complex dyes, like AG1, constitute a category of dyes used in several industries, including textile dyeing, leather finishing, inks, colouring for wood, metals and plastic. Their removal from industrial wastewaters has been given a lot of importance because of their toxicity and carcinogenic nature as well as their harm to the ecosystems (Hunger 2003). However, only a limited number of studies have been reported in the literature on this very important issue (Rizk and Hamed 2014).

The work presented in this paper focuses on the preparation and characterization of $[Zn-Al-Cl]$ -LDHs and their evaluation as scavengers of AG1 dye from aqueous solutions. The aim is to understand the mechanism of interaction between adsorbent and adsorbate for an eventual use of the system to remove such organic pollutant from textile effluents.

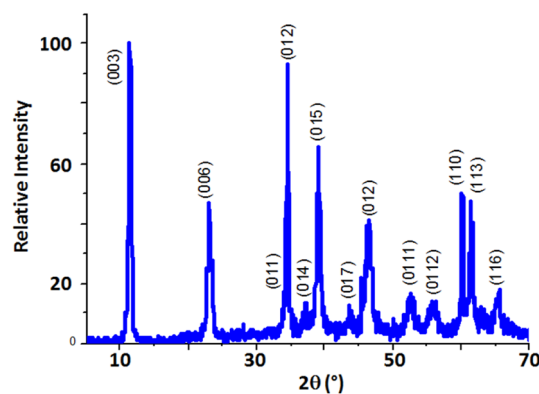


Fig. 1 XRD pattern of the $[Zn-Al-Cl]$ phase prepared by coprecipitation

Table 1 Experimental $[Zn]/[Al]$ ratio in the solid and its cell parameters

$[Zn]/[Al]_{th}$	$[Zn]/[Al]_{exp}$	a (nm)	c (nm)	$d = c/3$ (nm)
2.00	1.99	0.306	2.334	0.778

Materials and methods

Adsorbent preparation and characterization

All experiments were carried out under a stream of N_2 to avoid, or at least minimize contamination by atmospheric CO_2 . The $[Zn-Al-Cl]$ -LDH, with a $[Zn]/[Al]$ ratio of 2, was synthesized by coprecipitation at a constant pH of 9.0 and at room temperature. Mixtures of molar $ZnCl_2$ (97% Loba Chemie) and $AlCl_3$ (99% Loba Chemie) aqueous solutions were slowly introduced into the reactor at constant pH, maintained by simultaneous addition of a 0.1 M NaOH (98% Loba Chemie) solution. The resulting slurry was then stirred for 72 h at room temperature. It was then filtered, washed several times with decarbonated water and dried at room temperature (25 °C).

The material obtained is a pure LDH, as characterized by X-ray diffraction (XRD) (Fig. 1) (Miyata 1975). It consists of a well-crystallized single phase with large constituting crystallites. The experimental metal ratios and the lattice parameters, refined on the $R\bar{3}m$ space group, are given in Table 1.

Adsorbate

Acid Green 1 (DyStar Product-DA 40120) was used in its commercial form used in the textile industry. Some of its important properties are given in Table 2. A stock solution was prepared by dissolving 100 mg of AG1 in 1 L decarbonated water and was diluted in decarbonated water as needed. The maximum absorption wavelength of the dye

was determined to be $\lambda_{\max} = 650$ nm, using an SP-3000 Plus UV/Vis spectrophotometer in the 200–800 nm range. The calibration curve was controlled on a weekly basis to check the stability of the stock solution.

Retention experiments

Retention experiments were carried out by the batch equilibrium technique at room temperature (25 °C), constant pH, maintained by addition of NaOH, and under a stream of N_2 . Amounts of [Zn–Al–Cl] were dispersed in 100 mL AG1 solutions. The initial concentration of AG1 was varied between 0.05 and 1 g L^{-1} . After filtration, the solid products obtained were dried at room temperature. The quantity of AG1 retained by the LDH (Q) was calculated as the difference between initial and equilibrium concentrations of the dye (C_i and C_e , respectively) by mass of the adsorbent (m) in the volume of solution (V):

$$Q = (C_i - C_e) V / m.$$

Analytical techniques

The XRD equipment used was a Siemens D 501 diffractometer. Samples of unoriented powder were exposed to copper K_{α} radiation ($\lambda = 0.15415$ nm). Measurement conditions were 2 h range, 5°–70°, step size: 0.08° 2θ , and step counting time: 4 s. Data acquisition was effected on a DACO-MP microcomputer. Unit cell constants were calculated using a least squares refinement.

Absorbance IR spectra were recorded on a Perkin-Elmer 16 PC spectrophotometer, at a resolution of 2 cm^{-1} and averaging over 100 scans, in the range 400–4000 cm^{-1} . Samples were pressed into KBr discs.

TG and DTG studies were performed in air with a Setaram TG–DSC 92 instrument. Curves were recorded on 12 mg of the sample over a temperature range of up to 1200 °C at a heating rate of 5 °C min^{-1} . The weights were corrected for the small effect of the gas flow as a function of temperature.

Scanning electron microscopy (SEM) analysis of the LDH surface was performed using a Philips device. The observations are carried out at a voltage of 5 kV.

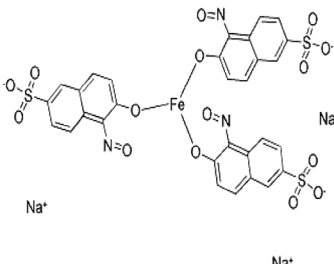
Results and discussion

Preliminary adsorption experiments were conducted to determine the optimal conditions for the retention of AG1 on LDHs regarding the pH value, contact time (t_c), initial adsorbate concentration (C_i) and the adsorbate/adsorbent mass ratio.

Effect of pH

Generally, pH is considered to be an important parameter that controls the retention at water–adsorbent interfaces ($m_{LDH} = 100$ mg, $C_i = 0.8$ g L^{-1} and $t_c = 48$ h). The retention of AG1 by [Zn–Al–Cl] was studied at different pH values ranging from 5 to 10 (Fig. 2). It is shown that the AG1 retention is at its maximum in the pH value around 8. The low retention observed at lower pH values (< 7) may be attributed to a partial dissolution of the basic mineral matrix by acidic hydrolysis, which becomes more pronounced when the pH decreases (El Gaini et al. 2008b; Elkhatabi et al. 2013). The low adsorption observed at pH 9 may be explained by a competition with the carbonate ions for which the LDH is known to have a great affinity.

Table 2 Some properties of AG1 dye

Commercial name	Acid Green 1
Systematic Name	[Ferrate (3+),tris[5,6-dihydro-5-(hydroxyimino-kappa.N)-6-(oxo-kappa.O)-2-naphthalenesulfonato(2-)]-sodium (1:3)
Synonyms	Basacid vert 970, Naphthol Green B
Chemical structure	
Formula	$Na_3C_{30}H_{15}FeN_3O_{15}S_3$
Molecular weight	878 g mol^{-1}
Solubility in H_2O	30 g L^{-1}

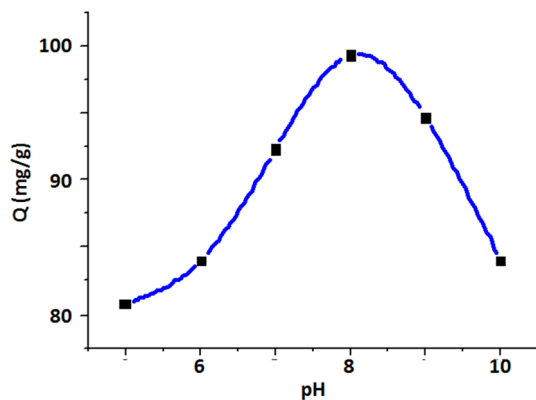


Fig. 2 Amounts of AG1 retained by [Zn–Al–Cl] at different pH values

The calibration of the medium (LDH + AG1) at relatively basic pH was carried out in air and is, therefore, susceptible to be contaminated by atmospheric CO_2 (Legrouri et al. 2005). This phenomenon takes place despite the precautions taken during the preparation of the solid sample and the kinetics study at high pH values. Following these experiments, it was decided to carry out the retention experiments at pH 8.

Effect of contact time

The amount of AG1 retained by [Zn–Al–Cl] as a function of solid–solution contact time, using an adsorbent mass of 100 mg with adsorbate initial concentrations between 50 and 200 mg L^{-1} , is shown in Fig. 3. The kinetic study shows that the retention equilibrium is reached after a contact time of 32 h for the highest concentration. This residence time was applied for the following retention experiments. A similar behaviour was obtained for other adsorbate with LDH materials (Elkhatabi et al. 2013; Legrouri et al. 2005; El Gaini et al. 2008a).

Kinetic models

Several models can be used to express the mechanism of solute adsorption onto an adsorbent. To design a fast and effective model, investigations were made on adsorption rates. Several kinetic models are used to test the experimental data for the examination of the controlling mechanisms of the adsorption process, such as chemical reaction, diffusion control and mass transfer. In this study, three kinetics models, namely the pseudo-first order, the pseudo-second order and the intra-particle diffusion were used to fit the experimental data from the adsorption of AG1 dye onto the LDH at pH 8 and initial dye concentrations of 50, 100 and 200 mg L^{-1} .

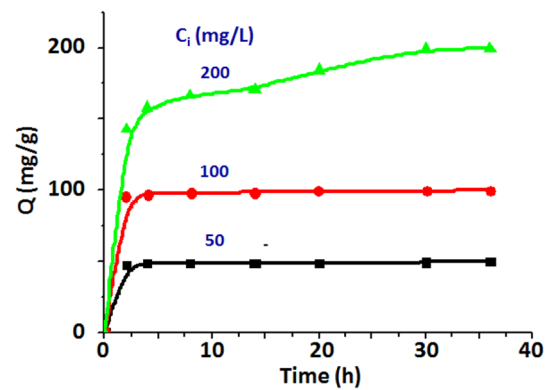


Fig. 3 Amounts of AG1 removed by 100 mg of [Zn–Al–Cl] versus contact time at various AG1 initial concentrations

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

Figure 4 presents the plots for the two models. For the pseudo-first-order model, a linear equation is obtained as follows:

$$\text{Log} (q_e - q_t) = \text{log } q_e - (K_1/2.303) \times t, \quad (1)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the sorption capacities at equilibrium and at time t , respectively, and k_1 (min^{-1}) is the rate constant.

The pseudo-second-order model is presented by the following equation:

$$t/q_t = 1/K_2 \times q_e^2 + (1/q_e) t, \quad (2)$$

where k_2 is the pseudo-second-order rate constant of adsorption ($\text{g mg}^{-1} \text{min}^{-1}$).

The analysis of the results reported in Table 3 shows that the AG1 retention kinetics by the LDH is in good agreement with the model of the pseudo-second order because the maximum amounts of experimental and theoretical adsorption data for the pseudo-first-order model are totally different. The experimental patterns are comparable with those of the pseudo-second order and the corresponding correlation coefficients are close to 1. The same result was obtained in a previous work (Elkhatabi et al. 2013).

Intra-particle diffusion model

To investigate the contribution of intra-particle behaviour on the adsorption process, the rate constant for intra-particle diffusion can be calculated from the following equation (Kang et al. 2013):

$$Q_t = k_{ip} t^{1/2} + C,$$

where k_{ip} is the intra-particle diffusion rate constant (mg g^{-1}) and C is the vertical axis intercept. If the plot of Q_t against

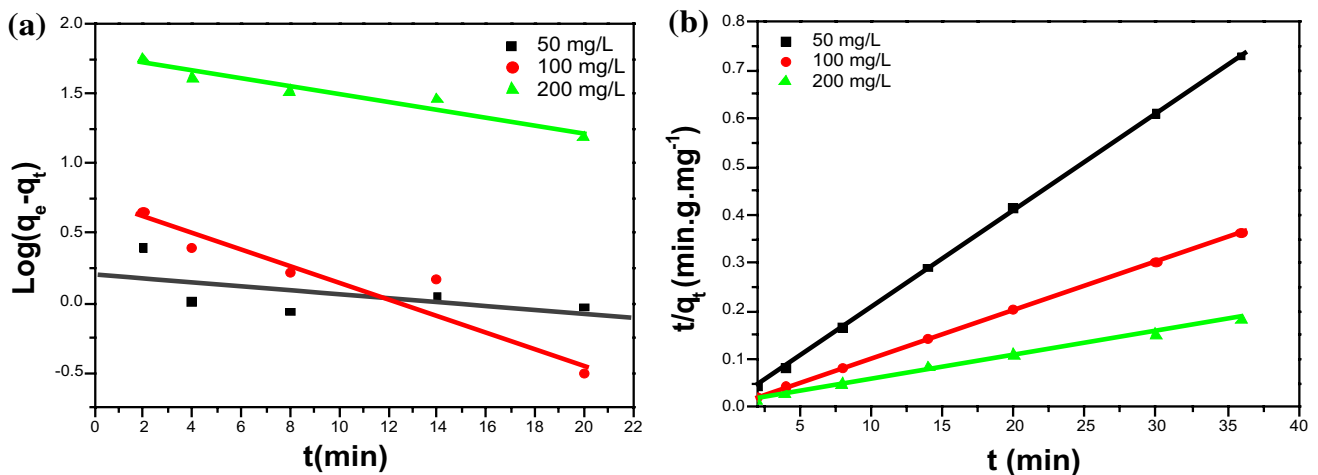


Fig. 4 Pseudo-first-order model (a) and pseudo-second-order model (b) plots for the adsorption of AG1 onto LDH at different initial dye concentrations

Table 3 Adsorption kinetics of AG1 dye on the LDH

[AG1] (mg L ⁻¹)	Pseudo-first order				Pseudo-second order			
	K ₁	Q _{e,th} (mg g ⁻¹)	Q _{e,exp} (mg g ⁻¹)	R ²	K ₂	Q _{e,th} (mg g ⁻¹)	Q _{e,exp} (mg g ⁻¹)	R ²
50	0.032	1.61	49.37	0.414	0.133	50	49.37	0.999
100	0.124	5.14	99.29	0.890	0.100	100	99.29	1.000
200	0.063	58.88	199.13	0.936	0.002	220	199.13	0.996

$t^{1/2}$ were linear, the adsorption process was deemed to have been determined by the intra-particle diffusion step.

Indeed, in this work, these lines correspond to the existence of the external diffusion process (external surface adsorption), followed by intra-particle diffusion and finally to a slow diffusion of the adsorbate to the micropores of the adsorbent (Yang et al. 2012).

The intra-particle diffusion model of AG1 adsorption onto LDH is shown in Fig. 5. For low concentrations (50 and 100 mg L⁻¹), it can be said that the diffusion mechanism of the adsorption system is described by two distinct regions instead of a single linear over the whole domain, which shows that the process has more than one step.

On the other hand, for the high concentration (200 mg L⁻¹), it is noted that the diffusion mechanism of the adsorption system is described by three distinct regions. The intermediate step is evident.

For the intra-particle diffusion, most curves show three linearities (Ofomaja 2010):

- Area I: adsorption on the surface.
- Area II: intra-particle diffusion (intercalation between the layers of the LDH phase).
- Area III: saturation (steady state).

The constants for intra-particle diffusion are listed in Table 4.

Adsorption isotherms

Figure 6 displays the retention isotherms of AG1 onto 30, 50 and 75 mg of LDH. Several models, such as Freundlich, Elovich, and Dubinin–Radushkevich, were tried on our data but only the Langmuir model gave good results. Therefore, the isotherms were fitted by Langmuir equation and can clearly be considered as pure L-type. They indicate that the interaction sorbate–sorbent is much stronger than solvent–sorbent at the adsorption sites. Isotherms with this profile are typical of systems where the functional adsorbate is strongly attracted by the adsorbent, mostly by ion–ion interaction, which tends to reach a saturation value given by a nearly isotherm plateau. These results again suggest that AG1 anions are preferentially removed.

As may be seen, the AG1 retention is inversely proportional to the mass of LDH. The Q_m value increases when the LDH mass decreases; this is somehow normal if we know that the retention of AG1 by the LDH can be done, in addition to adsorption, also by intercalation between the layers. This intercalation requires an increasing molar ratio (AG1/LDH) and, therefore, relatively small mass of LDH to allow maximum exchange of the chloride ions by the AG1 ions.

Fig. 5 Intra-particle diffusion kinetic for adsorption of AG1 ions on LDH

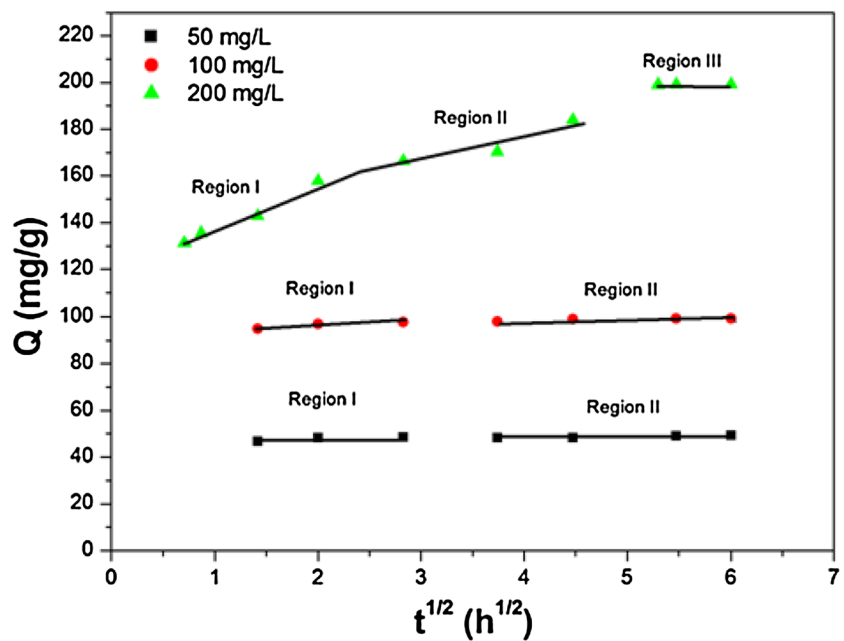


Table 4 Rate constants and correlation coefficients for intra-particle diffusion for adsorption of AG1 on LDH

C_0 (mg L ⁻¹)	Region I			Region II			Region III		
	k_{1P} (mg g ⁻¹ h ^{-1/2})	R^2	b_1 (mg g ⁻¹)	k_{2P} (mg g ⁻¹ h ^{-1/2})	R^2	b_2 (mg g ⁻¹)	k_{3P} (mg g ⁻¹ h ^{-1/2})	R^2	b_3 (mg g ⁻¹)
50	1.090	0.861	45.63	0.532	0.980	46.21			
100	1.928	0.950	92.41	0.586	0.890	95.91			
200	19.720	0.991	117.18	10.401	0.930	135.21	0.133	1	198.32

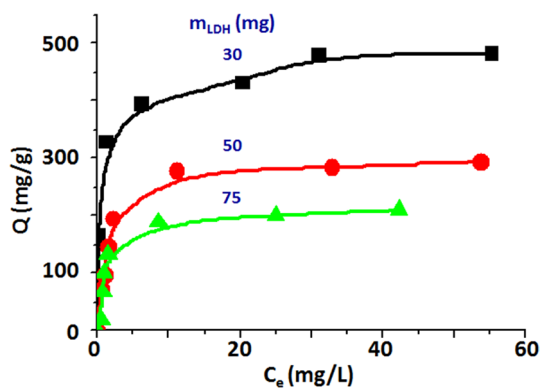


Fig. 6 Adsorption isotherms for AG1 determined with three different sorbing doses (30, 50 and 75 mg)

The data for the uptake of AG1 have been processed in accordance with the linear form of Langmuir isotherm equation:

$$C_e/Q = 1/Q_m \cdot K + C_e/Q_m,$$

where Q is the quantity of AG1 retained by the unit mass of LDH (mg g⁻¹), Q_m the maximum quantity of AG1 retained

by the unit mass of LDH (mg g⁻¹), C_e the equilibrium concentration of AG1 (mg L⁻¹) and K is the affinity constant of AG1 for LDH (L mg⁻¹).

A linear relationship was observed among the plotted parameters (Fig. 7), which indicates the applicability of the Langmuir's equation. The sorption parameters obtained are summarized in Table 5.

This linearization was used to standardize the method of determining the maximum quantity Q_m , which decreases when the mass of LDH is increased.

Effect of mass ratio AG1/LDH

The XRD of the solids obtained by ion exchange of chloride by AG1 corresponds to that of a hydrotalcite-type material. Figure 8 shows the XRD patterns for [Zn–Al–AG1]-LDHs prepared with different mass ratio AG1/LDH.

The layered structure of the material is preserved after intercalation. However, the crystallinity is lowered, as attested by the broadening of the lines and the decrease in their intensity. In addition, intercalation is observed to cause a displacement of the (003) line, denoting an increase in the interlayer space which is due to the exchange of the chloride

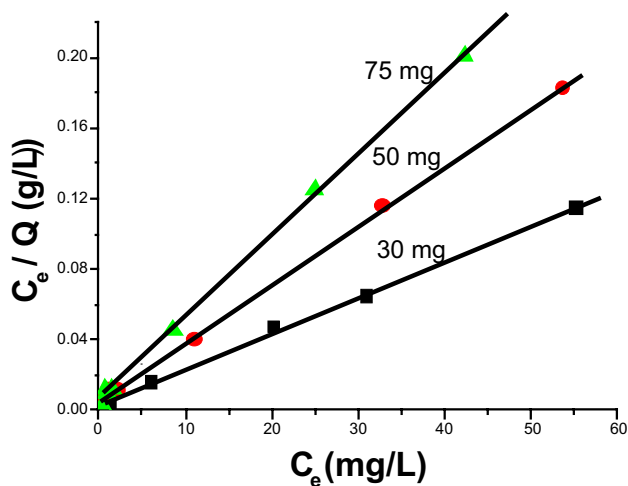


Fig. 7 Linearization curves with three different sorbing doses (30, 50 and 75 mg)

Table 5 Langmuir parameters for AG1 retention by the [Zn–Al–Cl]-LDH

M_{LDH} (mg)	Q_m (mg g ⁻¹)	K (L mg ⁻¹)	R^2
30	485.4	1.170	0.998
50	301.2	0.623	0.999
75	213.7	0.949	0.999

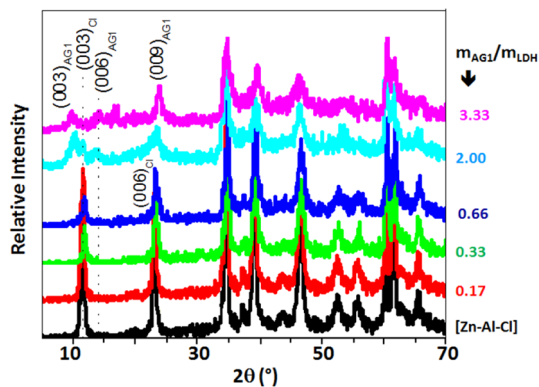


Fig. 8 XRD patterns of the phases obtained after retention of AG1 at different mass ratio AG1/LDH

by the larger AG1 ions. Furthermore, the adsorption on the surface does not affect this distance for low concentrations of the dye. By contrast, for relatively high concentrations, increased interlayer distance means that there is an exchange between chloride ions and the anions of AG1, which are larger and accompanied by the maximum occupancy of the available anionic sites.

The cell parameters for the best compound, in terms of crystallinity, were $a = 0.306$ nm, $c = 2.934$ nm and the

interlayer distance $d = 0.978$ nm. The study of the effect of mass ratio AG1/LDH indicates the existence of two phases, in terms of crystallinity, for $m_{AG1}/m_{LDH} = 2$ (Fig. 8). The presence of the line at $d = 0.778$ nm indicates that the exchange is only partial in this case. In addition, the interlayer distance varies slightly with the mass ratio AG1/LDH.

The observation shows that the maximum AG1 removed decreases when the mass of LDH is increased, which may seem strange but can be considered as normal with regard to the ion-exchange ability of the LDH. In fact, the ion exchange was observed to be requiring a high mass ratio ($m_{AG1}/m_{LDH} \geq 2$) and consequently a relatively low mass of the LDH allows for better ion exchange. It seems that this value corresponds to the optimum concentration of AG1 that is required to displace the chloride ions from within the LDH interlayer space. For mass ratios $AG1/[Zn-Al-Cl] < 2$ (Fig. 8), the interlayer distance remains equal to that of the initial matrix which means that retention is only done by adsorption to the surface. In contrast, when this ratio is higher than two, XRD patterns present another line at low 2θ values. This line corresponds to a distance of 0.978 nm, which proves the presence of a second phase intercalated by AG1 ions that are larger than chloride ($d = 0.778$ nm). This means that the increase in the concentration of AG1 and, therefore, the mass ratio (AG1/LDH) facilitates the exchange reactions with a large amount of chloride ions by the anions of dye.

Under these conditions, we can conclude that the elimination of the dye occurred according to two different processes:

- $AG1/[Zn-Al-Cl] < 2$: retention by adsorption on the surface.
- $AG1/[Zn-Al-Cl] \geq 2$: both adsorption and intercalation between the layers.

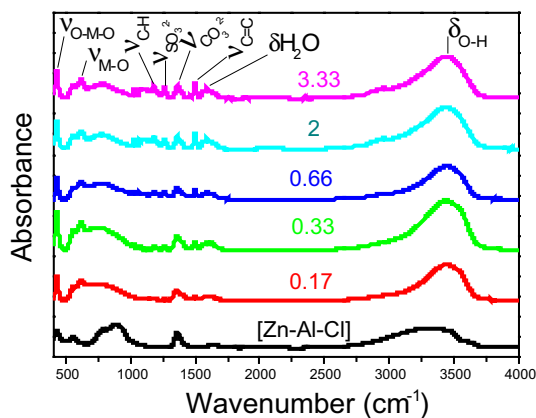
The retention of AG1 by the LDH attained 100% for a mass ratio equal to 0.66 (485.4 mg g⁻¹). This value is very good compared to results obtained by other researchers on the adsorption of some dyes by different materials (Table 6). This confirms the choice of LDH materials for the removal of such pollutants from water.

Infrared spectroscopy

The IR spectra of the phases, obtained following AG1-LDH interaction, are characteristic of LDH phases (Fig. 9). They are different from that of the parent material [Zn–Al–Cl] and present the bands reflecting the retention of AG1. The broad adsorption band around 3400 cm⁻¹ is due to the stretching of O–H groups of the hydroxide layer and interlayer water. In the low-frequency region, the bands at 809, 601 and 451 cm⁻¹ are ascribed to the lattice vibration modes attributed to the vibrations associated with the bonding of Zn

Table 6 Maximum capacities and dye removal percentages by different materials

Materials	Dyes	Q_m (mg g ⁻¹)	Retention (%)	References
[Zn–Al–Cl]	Methyl Orange	2455.315	–	Mahjoubi et al. (2016)
[Zn–Al–CO ₃]		1684.170	–	
[Zn–Al–NO ₃]		2270.576	–	
[Zn–Al–SO ₄]		2758.139	–	
[Zn ₂ –Al–Cl]	Remazol Blue 19	2187	100	Elkhatabi et al. (2013)
[Mg–Al–CO ₃]	Remazol Blue 19	350	76.35	Alexandrica et al. (2015)
[Cu–Al–CO ₃]	Evans Blue	95	79.91	Kefif et al. (2011)
[Co–Al–CO ₃]		99	76.62	
Pineapple leaf powder	Remazol Brilliant Blue R (RBBR)	42.03	96.2	Rahmat et al. (2016)
Lime peel powder	RBBR	39.37	95.9	
Orange peel	RBBR	11.62	–	Mafra et al. (2013)
Potato peel	Methylene Blue	32.7	87.6	Boumchita et al. (2016)
Corn cob	Methylene Blue	46.28	96	Miyah et al. (2016)
<i>Rhodotorula glutinis</i> biomass	AG1	476.2	–	Saravanan et al. (2012)
Activated carbon	AG25	182.6	–	Parimalam et al. (2012)

**Fig. 9** IR spectra of phases obtained after retention of AG1 by 30 mg of [Zn–Al–Cl] at different mass ratio AG1/LDH

and Al metals with oxygen—M–O and M–O–M (Hernandez-Moreno et al. 1985; Thorpe and Solin 1995; Legrouri et al. 2005). The asymmetric stretching vibration $\nu(\text{SO}_3^{2-})$ appears in the 1255 cm^{-1} . The absorption band at 1500 cm^{-1} is assigned to the stretching vibration of C=C in an aromatic ring. The band at 1180 cm^{-1} is assigned to the bending vibration C–H out of the benzene's cycle. Those at 1640, 1300 and 1188 cm^{-1} correspond to the C=O, C–O and C–N vibrations, respectively (Pouchert 1975; Pavia et al. 1996).

TG and DTG analyses

TG and DTG curves obtained for pure AG1, [Zn–Al–AG1] and [Zn–Al–Cl] are reported in Fig. 10. The thermogram of [Zn–Al–AG1] is different from that of [Zn–Al–Cl], which confirms the retention of AG1. The thermal evolution under air takes place in six consecutive stages with weight losses

for which the inflexion points coincide with temperatures corresponding to minima and maxima in the DTG trace. The first weight loss which begins as soon as heating is applied with a first effect at $85 \text{ }^\circ\text{C}$ is attributed to the loss of adsorbed water molecules. The second weight loss at $200 \text{ }^\circ\text{C}$ is assigned to the interlayer water. The third weight loss around $300 \text{ }^\circ\text{C}$ is attributed to the dehydroxylation of the brucite-like layers. This destruction takes place at the same temperature as that for the starting matrix [Zn–Al–Cl] ($264 \text{ }^\circ\text{C}$). This can be explained by the thickness of the interlayer gallery, $d = 0.978 \text{ nm}$, which predicts an orientation for AG1 anions are parallel to sheets with a low rate of hydration. These three first stages are similar to those previously reported for hydrotalcite-like materials (Labajos and Rives 1996).

For the rest, there is a relative stabilization of the decomposition of the dye with a sharp variation of different weight percentages for each decomposition stage. It is noted that the different fragments from the encapsulated AG1 decompose at greater temperatures than those from free AG1. The LDH stabilizes AG1 and delays the combustion of adsorbed and intercalated molecules. In addition, the last loss takes place in two steps when the dye is intercalated between the layers. It probably corresponds to the elimination of a fragment, which contains sulphur in the form of SO_2 because of its slow diffusion in the oxide matrix (Lakraimi et al. 2006).

The rest of the decomposition, which represents more than 30% of the total mass of [Zn–Al–AG1], leads to the formation of mixed oxides, ZnO, ZnAl_2O_4 , Fe_3O_4 and Fe_2O_3 , as shown in Fig. 11.

The thermal analyses confirm the retention of AG1 by the LDH via adsorption and intercalation, in agreement with the results obtained by the other characterization techniques [XDR and Fourier transform infrared spectroscopy (FTIR)].

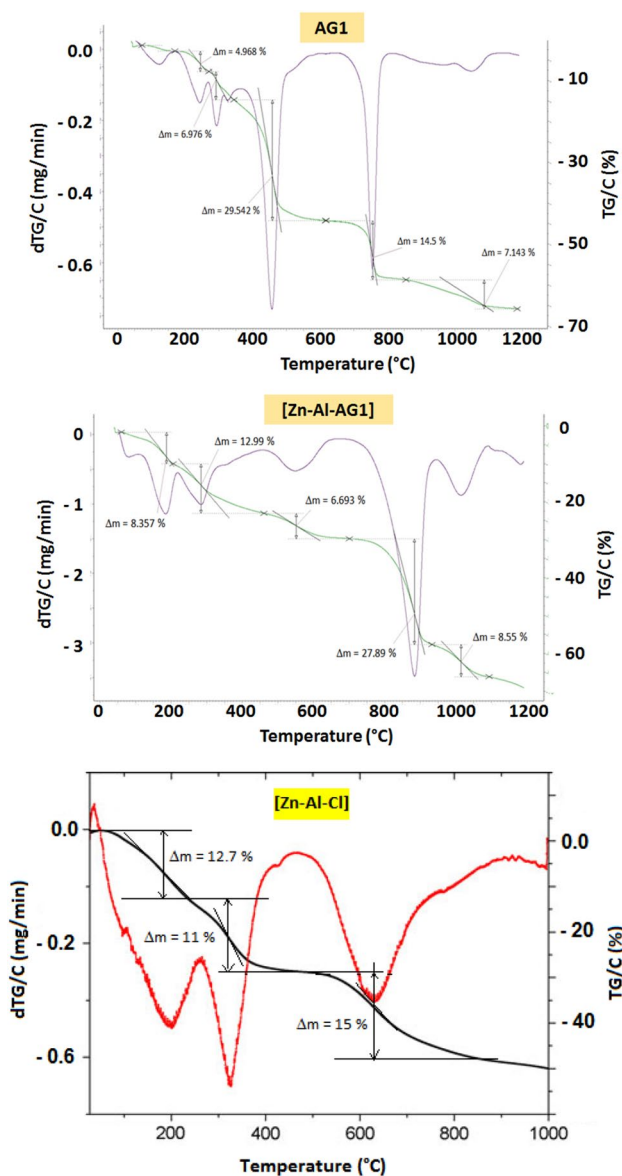


Fig. 10 TG and DTG curves obtained for pure AG1, [Zn-Al-AG1] and [Zn-Al-Cl]

Scanning electron microscopy

The SEM observation of the parent and the AG1-intercalated materials shows aggregates of crystallites formed perpendicular to the image plane (Fig. 12). The crystals present almost the same morphological features. They tend to result from the superposition of several leaflets with dimensions of the particles being about 2 μm for [Zn-Al-Cl] and lower than 2 μm for [Zn-Al-AG1]. The small morphological alteration of the layers, after exchange, can be due to the decrease in crystallinity observed by XRD in the samples.

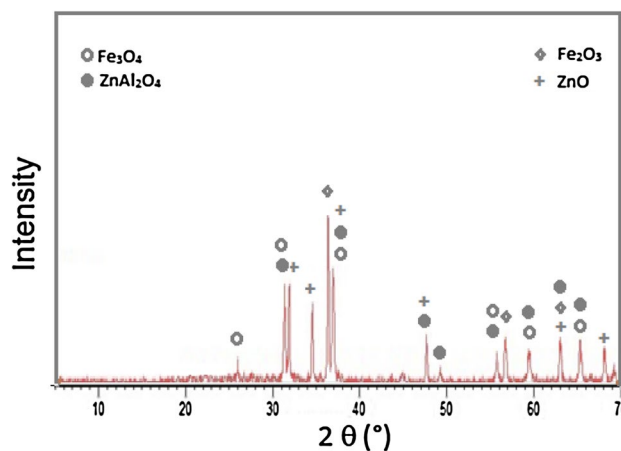


Fig. 11 XRD pattern of the phase [Zn-Al-AG1] calcined at 1200 °C

Structural model

Before proposing an orientation of the AG1 anion between the layers, we determined the value of the length of the molecule AG1 by molecular orbital semi-empirical method with the Gaussian 03 software, the calculated value for a horizontal position is 0.22 nm. Figure 13 shows the orientation of AG1 dye intercalated between LDH sheets.

The interlayer distance determined experimentally, 0.978 nm, suggests a horizontal direction (parallel to the planes of the layers) of the anion in the interlayer space:

$$d = 0.22 + 0.27 + 0.27 + 0.21 = 0.97 \text{ nm.}$$

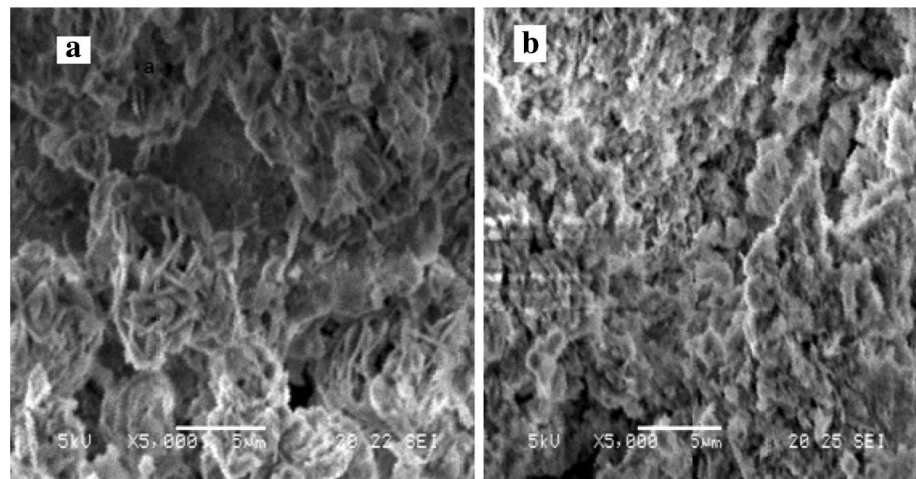
The adoption of a horizontal orientation for simple or large organic molecules has been proposed by other authors for porphyrins ($d = 1.17 \text{ nm}$) (Bonnet et al. 1998), oxalates ($d = 0.778 \text{ nm}$), aluminium oxalates ($d = 0.99 \text{ nm}$) and hydroxyl terephthalates ($d = 1.08 \text{ nm}$) (Prevot 1999).

Conclusions

The research activity focused on the removal of the textile dye AG1 by [Zn-Al-Cl]-LDHs from aqueous solutions. The LDH was prepared by coprecipitation and characterized by several physico-chemical techniques. Its retention of AG1 was observed to be important and occurs during the first hours of interaction. The equilibrium was reached after 2 h of contact and corresponds to an almost complete AG1 elimination for low concentrations.

The influence of various experimental parameters was studied to better understand and improve the retention process. These have resulted in the following satisfactory results:

Fig. 12 SEM photographs of [Zn–Al–Cl] (a) and [Zn–Al–AG1] (b)



- A high AG1/LDH proportion leads to an improved retention performance.
- The pH of the solution influences the ability of the LDH for the dye retention, with an optimal value of pH 8.
- Several models, such as Freundlich, Elovich, and Dubinin–Radushkevich, were tried on our experimental data but our adsorption isotherms could only be described by the Langmuir equation.
- The retention of the dye is due to adsorption for low AG1 concentrations. Both adsorption and intercalation in the interlayer space were observed for high concentrations.
- The Cl–AG1 exchange is proven by an increase in the interlayer space observed by XRD and the presence of AG1 functional groups in IR spectra and thermograms.
- Thermal analyses of the phase obtained after retention indicates that the LDH plays a stabilizing role and com-

bustion retardant for AG1. The final product is a mixture of oxides that may be used as catalysts.

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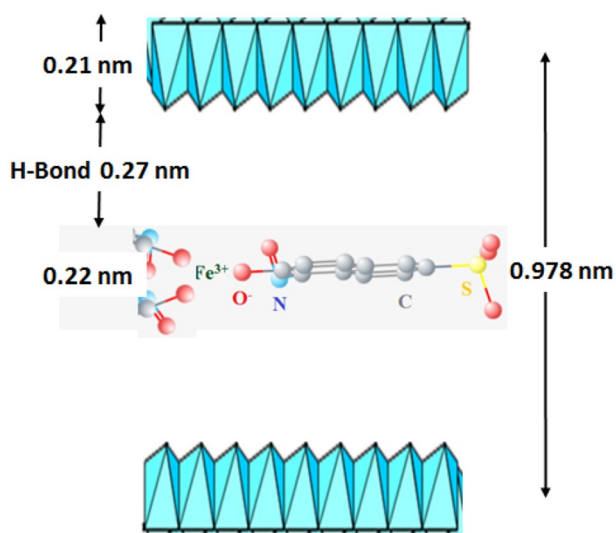


Fig. 13 The schematic illustration of AG1 intercalation between the LDH layers

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