Study of the adsorption process of textile dye AG1 by a mixed oxide derivative of anionic clay

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Abstract
Layered double hydroxides (LDH) are anionic clays with high anion exchange capacities. Calcination of LDH increases significantly their retention capacities. In the present study, calcined products (CLDH) were obtained by heating [Zn\(_{2}\)-Al-CO\(_3\)] at 500°C. The adsorption of the textile dye Acid Green 1 (AG1) by CLDH was performed at different pH values, the textile dye-adsorbent contact time and mass ratio AG1/CLDH. The equilibrium at room temperature is reached after 24 h, this is confirmed by rapid kinetic modeling of the experimental data by the pseudo-second order model. The adsorption is described by Langmuir-type isotherm. The study of adsorption isotherms, comparison with the retention of a carbonated phase of calcined and uncalcined, reveals that the first could be a good candidate for trapping such pollutants. Characterization of the CLDH solids, both fresh and after removal of AG1 by X-ray diffraction and infrared spectroscopy shows that the adsorption is also enhanced by reconstruction of a matrix hydrotalcite intercalated by AG1 at high concentration. The removal of textile dye in anionic form by CLDH gave satisfactory results. Under optimum conditions, the retention is total (100%) when the weight ratio AG1/CLDH is between 0.38 and 0.68. Retention capacity reached 800 mg/g.

Keywords: Calcined layered double hydroxides, Acid Green 1, Adsorption, Intercalation, Reconstruction.
1. Introduction

Different pollutants significantly harm our environment such dyes. Indeed, synthetic organic dyes are compounds used in many industrial sectors such as the automotive, chemical, paper and especially the textile sector where all the nuances and ranges of chemical families are represented. The affinities between the textile and the dyes vary depending on the chemical structure of dyes and the type of fibers on which they are applied. It is not uncommon to find that during the dyeing process, 15 to 20% of colorants, and sometimes up to 40% for sulfur and reactive dyes are discharged with the wastewater which is mostly directly discharged into rivers without treatment [1]. In recent years, studies on the textile dyes have shown that they are among the most toxic elements, and are also generally carcinogenic to living beings. Their removal is considered as important as the removal of soluble colorless chemical contaminants [2]. Different methods have been used in recent years to remove dyes [3-6]. Adsorption is one of the treatment processes, the most common in the clean water, and became an analytical method of choice, very effective and simple in use [7-10]. The work done during this study fits within the general framework of wastewater treatment. It was aimed to study the performance of an anionic clay calcined [Zn-Al-CO₃] (CLDH) on the aqueous medium holding textile dye namely Acid Green 1 (AG1). Our goal is to demonstrate the effectiveness of this method for the removal of this pollutant and optimize experimental parameters such as contact time, pH of aqueous solutions and mass ratio pollutant/CLDH. Adsorption on different solid materials, such as soils, clays and activated carbons, has been used by several investigators to eliminate the textile dyes from water samples. Layered double hydroxides (LDH), also known as hydrotalcite-like compounds or anionic clays and their calcined products (CLDH), have been widely used as adsorbent [11-15]. LDH are layered materials with hydroxide sheets, where a net positive charge is developed on the layer due to partial substitution of trivalent for divalent cations, balanced by exchangeable charge compensating anions and water molecules, which are present in the interlayer space [14]. They can be represented by the general formula [16]:

\[ [\text{M}^\text{II}_{1-x}\text{M}^\text{III}_x(\text{OH})_2](\text{An}^-)_{n/2} \text{mH}_2\text{O}, \text{ abbreviated as } [\text{M}^\text{II}_x - \text{M}^\text{III}_1 - \text{A}] \]

With R = [MII]/[MIII], where MII is divalent cation like Mg²⁺, Zn²⁺, Cu²⁺, etc., MIII trivalent cations like Al³⁺, Cr³⁺, Fe³⁺, etc., An⁻ interlayer anion and x is defined as the MII/(MII + MIII) ratio.

Calcined [Zn₂-Al-CO₃] LDH have been demonstrated to reconstruct their original layered structure after adsorption of various anions and are good ion exchangers/adsorbents for removal of toxic anions from contaminated water [14-18]. In the light of this so-called “memory effect” [17], removal of AG1 from aqueous solution by calcined [Zn₂-Al-CO₃] was studied in this work. The localization of the textile dye in the interlayer space and/or on external surfaces of the CLDH is studied by X-ray diffraction (XRD), as well as by infrared spectroscopy (IR).

2. Materials and methods

2.1. Preparation of [Zn₂-Al-CO₃]

The hydrotalcite-like compound (anionic clay) consists of brucitic sheets whose centers of octahedra are occupied by Zn and Al and the spaces between the sheets by the CO₃²⁻ anions and H₂O molecules. This material [Zn₂-Al-CO₃] was synthesized reproducibly by coprecipitation method [19] at constant pH = 10 as a metal ratio Zn/Al = 2 and a ripening time of 72 hours under mild agitation, then this material is calcined at a temperature of 500 °C during 5 h. The [Zn₂-Al-CO₃] was prepared starting from a mixture of metal salts solutions Zn(SO₄), 7H₂O 0.4M and AlCl₃, 6H₂O 0.4M and a solution containing 0.3M of Na₂CO₃ and 0.1M of NaOH. At the beginning, were added some drops of the mixture Na₂CO₃, NaOH at 250 ml of distilled water to bring back the pH to the value of synthesis pH = 10. The coprecipitation was performed by slow addition (2 mL/h) of mixture of metal salts. The precipitate was filtered, washed several times with distilled water and then dried at room temperature (25 °C).
2.2 Retention experiments

Retention experiments were carried out by the batch equilibrium technique at room temperature, at constant pH, maintained by addition of NaOH and under a stream of N\textsubscript{2} in order to avoid, or at least minimize, the contamination by atmospheric CO\textsubscript{2}. Amounts of CLDH were dispersed in 100 mL AG1 solutions. The initial concentration of AG1 was varied between 50 and 800 mg/L. After filtration, the solid products obtained were dried at ambient temperature before being analysed by XRD, IR and SEM. The supernatants were recovered and the residual dye concentration was determined by UV-Vis spectroscopy. The absorbance was measured at 620 nm on a SPECTRONIC GENESYS 5 spectrophotometer. The quantity of AG1 retained by the CLDH, Q, was calculated as the difference between initial and equilibrium (final) concentrations of the textile dye in solution (C\textsubscript{i} and C\textsubscript{e}, respectively) by mass of the sorbent (m) in the volume of solution, V:

\[ Q = (C_i - C_e)V /m. \]

2.3 Structural characterization techniques

The XRD equipment used was a Siemens D 501 diffractometer. Samples of unoriented powder were exposed to copper K\textsubscript{α} radiation (λ = 0.15415 nm). Measurement conditions were 2\textdegree\ range 5–70\textdegree, step size: 0.08-2\textdegree, and step counting time: 4 s. Data acquisition was effective 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\textsuperscript{-1} and averaging over 100 scans, in the range 400–4000 cm\textsuperscript{-1}. Samples were pressed into KBr discs. The Scanning Electron Microscopy (SEM) allows viewing the external morphology of materials. The principle of scanning is to scan the surface of the sample in successive rows and to transmit the sensor signal to a cathode ray tube whose scan is exactly synchronized with that of the incident beam. The scanning microscopes use a very fine beam which scans the surface point by point of the sample. The analysis of the outer surface of the LDH was performed using a Philips device. The observations are carried out at a voltage of 5 kV.

3. Results and discussion

3.1. Characterisation of [Zn\textsubscript{2}–Al–CO\textsubscript{3}]

3.1.1. X-ray diffraction

Characterization of the solid obtained by XRD (Fig. 1) showed that the phase corresponds to a pure LDH [20]. The solid consists of a well-crystallized single phase with large constituting crystallites. The lattice parameters refined on the hexagonal setting with a rhombohedral symmetry (space group: R \textbar \textbar \textbar 3m) and the experimental metal ratios are given in Table 1.

![Figure 1. XRD pattern of [Zn\textsubscript{2}–Al–CO\textsubscript{3}] LDH.](image)
Table 1. Experimental [Zn]/[Al] ratio in the solid and its cell parameters.

<table>
<thead>
<tr>
<th>[Zn]/[Al]&lt;sub&gt;th&lt;/sub&gt;</th>
<th>[Zn]/[Al]&lt;sub&gt;exp&lt;/sub&gt;</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>1.99</td>
<td>0.306</td>
<td>2.292</td>
<td>0.764</td>
</tr>
</tbody>
</table>

3.1.2. Infrared spectroscopy

The IR spectrum of the intercalated phase by carbonate anions (Fig. 2) shows bands at 3470 and 1630 cm<sup>-1</sup> corresponding respectively to the valence vibrations of hydroxyl groups of the brucite layers (ν<sub>OH</sub>) and deformation vibration of interlayer water molecules (δ<sub>H2O</sub>). It is important to note the presence of a shoulder at 3040 cm<sup>-1</sup> in this spectrum. Many authors have shown that this shoulder corresponding to a hydroxyl ion stretching vibration associated with carbonate anions by hydrogen bonds in pyroaurite type minerals [21-23]. The carbonate anion free said belongs to D<sub>3h</sub> symmetry group and only ν<sub>2</sub>, ν<sub>3</sub> and ν<sub>4</sub> vibrations respectively to 879, 1429-1492 and 706 cm<sup>-1</sup> are active in the infrared in a reference compound such as CaCO<sub>3</sub> [24,25]. However, the frequency of this vibration on the spectrum of [Zn<sub>2</sub>-Al-CO<sub>3</sub>] is lowered to a few tens of cm<sup>-1</sup> with respect to the observed frequencies CaCO<sub>3</sub> (1430 cm<sup>-1</sup>). We can deduce that the carbonate anions are not the same environment in both materials. In [Zn<sub>2</sub>-Al-CO<sub>3</sub>], although their symmetry seems to be close to D<sub>3h</sub> the carbonate anions are linked by hydrogen bonding with water molecules or hydroxyl ions interlayer sheets as confirmed by the presence of the shoulder in 3040 cm<sup>-1</sup> resulting in a displacement of the vibration ν<sub>3</sub> toward lower frequencies. The shoulder at 1480 cm<sup>-1</sup> and the appearance in the vicinity of 1050 cm<sup>-1</sup> band of the ν<sub>1</sub> show that some carbonate anions may exist in a different symmetry, the symmetry is lowered. Comparison with the vibration observed for reference compounds shows that these anions are monobonded to a metal cation (Zn, Al) in substitution of hydroxyl ion of sheets. We can report that the absorption bands that reflect the lowering of symmetry are relatively very low, which suggests that these monobonded carbonate anions are not inserted between the sheets but rather adsorbed on the surface of monocrystallites.

![IR spectra of [Zn<sub>2</sub>-Al-CO<sub>3</sub>].](image)

3.1.3. Scanning Electron Microscopy

The SEM image corresponding to the [Zn<sub>2</sub>-Al-CO<sub>3</sub>] phase is shown in Figure 3. The lamellar structure is well highlighted by the presence of crystallites which are distributed more homogeneously.
3.2. Adsorption equilibrium

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

3.2.1. Effect of pH

Generally pH is considered to be an important parameter that controls the adsorption at water-adsorbent interfaces. He fixed on the one hand, the degree of ionization of the acid functional groups or basic adsorbates and therefore controls the solution speciation and modifies the other hand, the surface charge of the support such as layered double hydroxides. Keeping this in view, the adsorption of AG1 on CLDH was studied at different pH values ranging from 5 to 10, which was depicted in Figure 4. It is shown that the dye adsorption on CLDH is at its maximum at pH between 6 and 7. The smaller adsorption observed at lower pH values may be attributed to a partial dissolution of the mineral matrix by acidic hydrolysis [26-28]. The low adsorption observed when pH increases may be explained by a competition with the carbonate ion for which the LDH is known to have a great affinity [12]. This phenomenon takes place despite the precautions taken during the preparation of the solid sample and the kinetics study when the pH value is high.

Figure 3. SEM phase [Zn$_2$-Al-CO$_3$].

Figure 4. Amount of AG1 retained by CLDH at different pH values \( (m_{CLDH} = 50 \text{ mg}, C_i = 200 \text{ mg/L}, t_c = 24 \text{ h}). \)
Thereafter all the experiments will be conducted at pH between 6 and 7, knowing that the AG1 dye is anionic form in aqueous solution.

### 3.2.2. Effect of contact time

The amount of AG1 adsorbed as a function of contact time, using a constant adsorbent mass of 50 mg and initial concentration of 200 mg/L is shown in Figure 5. The kinetic study shows that the adsorption equilibrium state is reached after a contact time of 24 h since no change in the adsorbed amount is detected afterwards. A similar behavior was obtained for pesticide 2,4-D with [Zn2-Al-CO3] calcined at 500 °C [29]. To be sure that the equilibrium state is reached for higher concentration, an AG1-CLDH contact time of 24 hours was applied in the retention experiments.

![Figure 5. Amount of AG1 (C_i = 200 mg/L) sorbed by 50 mg of CLDH versus contact time.](image)

### 3.3. Adsorption Kinetics

#### 3.3.1. Pseudo-first and pseudo-second order

It is known that the adsorption kinetics describes the order and the solute uptake rate governing the residence time of the adsorption reaction, is one of the most important characteristics that define the efficiency of adsorption. Figure 6 shows that the kinetic of AG1 adsorption onto CLDH. The adsorption of AG1 by CLDH is fast. The above adsorption kinetic experimental data can be best fitted into a pseudo-second order rate kinetic model. Different models were attempted to test the kinetics of interactions with CLDH and AG1 are expressed as follows:

\[
\ln (Q_e - Q_t) = \ln Q_e - k_1 t : \text{pseudo-first order} \quad [30]
\]

\[
t/Q_e = 1/(k_2Q_e^2) + (1/Q_e) t : \text{pseudo-second order} \quad [31]
\]

where \(Q_e\) and \(Q_t\) are the amount of AG1 adsorbed at equilibrium and at time \(t\), respectively. \(k_1\) and \(k_2\) are the rate constants of the pseudo-first and pseudo-second order models of adsorption. The pseudo second-order kinetic at different mass is plotted in Figure 6; \(k_2\) and \(Q_e\) calculated from the model are also listed in table 2 along with the corresponding correlation coefficient. When second-order kinetics is applied, the \(t/Q_e\) versus \(t\) plot is also linear and the second-order rate constant, \(k_2\), is 0.0009 g/mg/h for mass concentration 200 mg/L (Table 2). The predicted equilibrium adsorbed amount was close to the experimental value indicating the applicability of the pseudo-second order model and the value of the correlation coefficient \(R^2\) suggests that this model well represents the adsorption kinetics.
3.3.2. Intra-particle diffusion

To investigate the contribution of intra-particle behavior on the adsorption process, the rate constant for intra-particle diffusion can be calculated from the following equation [32,33]:

\[ Q_t = k_i t^{1/2} + C \]

where \( k_i \) is the intra-particle diffusion rate constant (mg/g), and \( C \) is the vertical axis intercept. If the plot of \( Q_t \) against \( t^{1/2} \) were linear, the adsorption process was deemed to have been determined by the intra-particle diffusion step. Additionally, intra-particle diffusion was the only rate-limiting step if the line tended to pass through the origin. Indeed, in recent 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 [34,35]. The intra-particle diffusion model of AG1 adsorption on the CLDH is shown in Figure 7. It may be noted that the diffusion mechanism of adsorption system is described by three distinct regions instead of linear over the entire domain implying that the process has more than one step. The intermediate step is evident. For the intra-particle diffusion, most curves show three linearities [36,37]:

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

The constants for intra-particle diffusion are listed in Table 3.

### Table 2. Adsorption kinetics describes the order and correlation coefficients for retention of AG1 by CLDH (\( C_i = 200 \) mg/L, \( m_{CLDH} = 50 \) mg).

<table>
<thead>
<tr>
<th>Pseudo-first order</th>
<th>Equation</th>
<th>( k_1 ) (h(^{-1}))</th>
<th>( Q_{e , th} ) (mg/g)</th>
<th>( Q_{e , exp} ) (mg/g)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \ln(Q_e - Q_0) = -0.0595^t + 3.7251 ]</td>
<td>+</td>
<td>0.0595</td>
<td>41.475</td>
<td>400</td>
<td>0.3721</td>
</tr>
<tr>
<td></td>
<td>3.7251</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pseudo-second order</th>
<th>Equation</th>
<th>( k_2 ) (g/mg/h)</th>
<th>( Q_{e , th} ) (mg/g)</th>
<th>( Q_{e , exp} ) (mg/g)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ t/Q_t = 0.0024^t + 0.0061 ]</td>
<td>+</td>
<td>0.000944</td>
<td>416.667</td>
<td>400</td>
<td>0.9987</td>
</tr>
<tr>
<td></td>
<td>0.0061</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 6.** Pseudo-first order model (a) and pseudo-second order model (b) for the kinetic adsorption of AG1 onto CLDH.
Figure 7. Intra-particle diffusion kinetic for adsorption of AG1 ions on CLDH.

Table 3. Rate constants and correlation coefficients for intra-particle diffusion.

<table>
<thead>
<tr>
<th>Area</th>
<th>Equation: $Q_t = k_{ip} t^{1/2} + C_i$</th>
<th>Area II</th>
<th>Equation: $Q_t = k_{2p} t^{1/2} + C_2$</th>
<th>Area III</th>
<th>Equation: $Q_t = k_{3p} t^{1/2} + C_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area I</td>
<td>$Q_t = 175 t^{1/2} - 93.146$</td>
<td>$Q_t = 33.836 t^{1/2} + 234.51$</td>
<td>$Q_t = 0.005 t^{1/2} + 399.89$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{ip}$ (mg/g/h$^{1/2}$)</td>
<td>$C_i$ (mg/g)</td>
<td>$R^2$</td>
<td>$k_{2p}$ (mg/g/h$^{1/2}$)</td>
<td>$C_2$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>175</td>
<td>-93.146</td>
<td>0.9751</td>
<td>33.836</td>
<td>234.51</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

3.4. Adsorption Isotherms

Figure 8 displays the retention isotherms of AG1 onto 50, 60 and 80 mg of CLDH. The AG1 adsorption isotherms on calcined [Zn$_2$-Al-CO$_3$] can be considered clearly as H-type, indicating that the interaction sorbate-sorbent is much stronger than solvent-sorbent at the adsorption sites (high affinity between AG1 and CLDH). 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.

Figure 8. Adsorption isotherms for AG1 determined with three different doses of CLDH (50, 60 and 80 mg) and uncalcined LDH.

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We note that the retention of Acid Green 1 is proportional to the mass of CLDH and than allure of these isotherms is Langmuir type. This proves that the retention of the pollutant is by reconstruction LDH phases intercalated by AG1. Retention by uncalcined \([\text{Zn}_2\text{-Al-CO}_3]\) is almost zero because of the greater affinity of carbonates for LDH. The data for the adsorption of AG1 have been processed in accordance with the linear form of Langmuir isotherm equation:

\[
C_e/Q = (1/KQ_m) + C_e/Q_m
\]

Q is the quantity of AG1 retained by the unit mass of CLDH (mg/g); \(Q_m\), the maximum quantity of AG1 retained by the unit mass of CLDH (mg/g); \(C_e\), the equilibrium concentration of AG1 (mg/L) and K is the affinity constant of AG1 for CLDH (L/g). A linear relationship was observed among the plotted parameters (Figure 9), which indicates the applicability of the Langmuir’s equation. The sorption parameters obtained are summarized in Table 4.

![Figure 9](image.png)

**Figure 9.** Linearization curves with three different sorbing doses (50, 60 and 80 mg).

**Table 4.** Langmuir isotherm model constants and correlation coefficients for retention of AG1 on CLDH.

<table>
<thead>
<tr>
<th>(m_{\text{CLDH}}) (mg)</th>
<th>(Q_m) (mg/g)</th>
<th>K (L/mg)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>515.68</td>
<td>0.072</td>
<td>0.9988</td>
</tr>
<tr>
<td>60</td>
<td>781.25</td>
<td>0.164</td>
<td>0.9889</td>
</tr>
<tr>
<td>80</td>
<td>800.00</td>
<td>0.450</td>
<td>0.9966</td>
</tr>
</tbody>
</table>

Note that the K values are relatively comparable, which lets us advance the type of interaction between the adsorbed molecule AG1 and the CLDH surface is the same regardless of the mass of CLDH used. By against the values of \(Q_m\) vary depending on the mass. These results are confirmed by other analytical techniques (XRD, IR and SEM) for products obtained after retention.

### 3.5. Study by X-ray diffraction

The solid compounds collected after contact with the solution of the dye AG1 for different mass ratios AG1/CLDH were analyzed by XRD. The spectra of the phases obtained are shown in figure 10. The LDH diffractograms \(X\) obtained after retention varying amounts of AG1 indicate that these phases correspond to hydrotalcite-like materials. However, the crystallinity of reconstructed phases is lowered; this is detected by peak broadening and the decrease of their intensities. For mass ratios AG1/CLDH lower or equal to 1.16, there is the reconstruction of two phases, one
intercalated by carbonates of whose interlamellar distance is 0.764 nm and the other by the AG1 dye with \( d = 0.98 \) nm. One can argue that for such reports, there is competition between the dye anions and carbonate anions to the reconstructed LDH sheets. Contamination from carbonates during the LDH rehydration experiments was inevitable and probably the amount of AG1 was not sufficient to limit it. By cons when the mass ratio AG1/CLDH is greater than or equal to 1.33, there is disappearance of the line (003) characteristic of the phase intercalated by carbonates. That is to say that we are witnessing the reconstruction of a single phase intercalated by AG1 dye. The amount of dye in this case is probably sufficient to minimize the intercalation of carbonates. We can conclude that for these domains of mass ratios, the AG1 retention is done in two ways: adsorption on the surface and intercalated between the layers of the reconstructed matrix. The removal of textile dye in anionic form by CLDH gave satisfactory results. Under optimum conditions, the retention is total (100%) when the mass ratio AG1/CLDH is between 0.38 and 0.68. Retention capacity reached 800 mg/g for AG1. This value is higher compared to the removal of AG1 from an aqueous solution using dried Rhodoturula glutinis that attained 476.2 mg/g [38] and greater than the one that is obtained when the retention AG25 by an activated carbon which in the region of 182.6 mg/g [39].

The lattice parameters for that phase intercalated by AG1 \([\text{Zn}_2\text{-Al-AG1}]\) are: \( a = 0.306 \) nm, \( c = 2.94 \) nm and the interlayer distance \( d = 0.98 \) nm.

![Figure 10. XRD patterns of the phases obtained after retention of AG1 at different mass ratios \( \frac{m_{AG1}}{m_{CLDH}} \).](image)

**3.6. Study by infrared spectroscopy**

The results obtained by infrared spectroscopy for \([\text{Zn}_2\text{-Al-AG1}]\) \( (\frac{m_{AG1}}{m_{CLDH}} = 1.33) \) are in agreement with those of XRD, they clearly confirm the characteristic bands of AG1 (Figure 11). Broadband and intense to 3400 cm\(^{-1}\) corresponds to OH stretching vibrations. The band appearing at 1628 cm\(^{-1}\) revealed the O-H bending mode of the water molecules. The bands revealed the presence of hydroxyl ions arising from the brucite-layers. The band at 1360 cm\(^{-1}\) was attributed to the characteristic vibrations of carbonate contamination. The characteristic vibrations of AG1 located around 1500 cm\(^{-1}\), they correspond to the bonds of C=C vibrations of the benzene ring. In the region between 1100 and 1260 cm\(^{-1}\) is observed symmetric and asymmetric vibration sulfonate groups, which shows that the AG1 retention is by interaction between sulfonate groups of the intercalated dye and the hydroxyl groups of the reconstructed layers (LDH phase). Bands between 700 and 800 cm\(^{-1}\) correspond to vibration (C-H) out of deformation benzene rings. Bands at 1640, 1300 and 1188 cm\(^{-1}\) respectively correspond to the vibrations C=O, C-O and C-N. We also note that the characteristic vibrations of LDH sheets (around 430 and 638 cm\(^{-1}\)) were observed with apparent intensities [12].
3.7. Analysis by Scanning Electron Microscopy

The sample shows aggregates of crystallites formed perpendicular to the image plane (Figure 12). The SEM of [Zn$_2$-Al-CO$_3$] calcined at 500 °C and that of [Zn$_2$-Al-AG1] were made at a magnification of 10000 times. For the calcined matrix, it presents sizes of relatively smaller particles and non-uniformity due to the destruction of the lamellar character of our material. We are also witnessing the emergence of the image of a mottled appearance of some crystallites or even some agglomerates. These can correspond to the segregation of mixed oxides [29,40]. The lamellar character of the intercalated compound by the dye [Zn$_2$-Al-AG1] appears obvious, which shows a reconstruction of a hydrotalcite phase. The sample shows aggregates consisting of crystallites resulting from the superposition of layers. These crystallites are of different sizes and may be up to 2 μm. The crystalline organization is relatively lower compared to that of the uncalcined matrix [Zn$_2$-Al-CO$_3$], this result is confirmed by the diffraction patterns of the two compounds.

![Figure 12. SEM photographs of calcined [Zn$_2$-Al-CO$_3$] (a) and [Zn$_2$-Al-AG1] (b).](image)

3.8. Structural model

Before proposing an orientation of the anion AG1 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. The figure 13 shows the orientation of AG1 dye intercalated between LDH sheets.

The interlamellar distance determined experimentally, that is 0.98 nm, suggesting a horizontal direction (parallel to the planes of the layers) of the anion in the interlayer space AG1:

d = 0.11 + 0.11 + 0.27 + 0.27 + 0.21 = 0.97 nm \sim 0.98 \text{ nm}.

The adoption of a horizontal orientation, parallel to the LDH sheets for simple or large organic molecules has been proposed by other authors, as porphyrins with d = 1.17 nm [40], the oxalates with d = 0.778 nm, oxalates aluminum with d = 0.99 nm or hydroxytéréphtalates with d = 1.08 nm [41,42].
4. Conclusion

The kinetic study reflects a high affinity of CLDH material for the textile dye AG1. The equilibrium at room temperature is reached after 24 h. This is confirmed by kinetic modeling of the experimental data by the pseudo second-order model which involves chemisorption mechanism. The adsorption capacity depends on the initial pH of the solution. To pH greater than 7 or less than 6, there is a decrease in the amount retained respectively due to contamination with the carbonate ions and the partial dissolution of the matrix. However, maximum retention is obtained with an optimum pH between 6 and 7 for AG1. The study of adsorption isotherms, comparison with the retention of a carbonated phase of calcined and uncalcined, reveals that the first could be a good candidate for trapping such pollutants. The amount adsorbed of the textile dye depends on the mass ratio AG1/CLDH. The results of XRD and IR indicate that the retention is governed by adsorption textile dye on sites available on the surface of the reconstructed LDH phases ([Zn-Al-CO$_3$] and [Zn-Al-AG1]) and by intercalation between the layers of the reconstructed LDH phase [Zn-Al-AG1]. Rehydration of mixed oxides formed after calcination (500°C) of the starting material in the presence of pollutants gives a reconstruction of hydrotalcite phase with preservation of lamellar character (XRD, SEM). The removal of dye in anionic form by CLDH gave satisfactory results. Under optimum conditions, the retention is total (100%) when the mass ratio AG1/CLDH is between 0.38 and 0.68 for AG1. Retention capacity reached 800 mg/g.

References