



## Review

Removal of indigo carmine dye from water to Mg–Al–CO<sub>3</sub>-calcined layered double hydroxidesL. El Gaini<sup>a</sup>, M. Lakraimi<sup>b</sup>, E. Sebbar<sup>a</sup>, A. Meghea<sup>c</sup>, M. Bakasse<sup>a,\*</sup><sup>a</sup> Faculty of Science, University Chouaib Doukkali, 24000 El Jadida, Morocco<sup>b</sup> ENS Ecole Normale Supérieure, 40000 Marrakech, Morocco<sup>c</sup> University POLITEHNICA of Bucharest, Romania

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## ABSTRACT

Layered double hydroxides (LDHs) calcined, denoted as CLDHs, have been shown to recover their original layered structure in the presence of appropriate anions. In the light of this so-called “memory effect”, the removal of indigo carmine (IC), an anionic dye, from aqueous solution by calcined Mg–Al–CO<sub>3</sub> LDHs was investigated in batch mode. We looked at the influence of pH values, dye-adsorbent contact time, initial dye concentration and various temperatures of heating of LDHs on the decolorization rate of IC. The adsorption isotherms, described by Freundlich model are L-type. The characterization of the solids CLDHs, both fresh and after removal of IC, by X-ray diffraction and infrared spectroscopy shows that the IC adsorption on CLDHs is enhanced by reconstruction of a matrix hydrotalcite intercalated by the dye, and the intercalation of the organic ion was clearly evidenced by the net increase in the basal spacing from 0.76 nm for [Mg–Al–CO<sub>3</sub>] to 2.13 nm for the organic derivative.

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## Contents

1. Introduction .....	627
2. Materials and methods .....	628
2.1. Preparation of [Mg–Al–CO <sub>3</sub> ] .....	628
2.2. Retention experiments .....	628
2.3. Structural characterization techniques .....	628
3. Results and discussion .....	628
3.1. Characterization of [Mg–Al–CO <sub>3</sub> ] .....	628
3.1.1. X-ray diffraction .....	628
3.1.2. Infrared spectroscopy .....	629
3.2. Effect of pH .....	629
3.3. Effect of contact time .....	630
3.4. Adsorption isotherms .....	630
3.5. Mechanism of removal of IC .....	630
4. Conclusion .....	632
References .....	632

## 1. Introduction

Controlling pollution is the main concern of society today. Large amounts of dyes are annually produced and used in textile, cosmetics, paper, leather, pharmaceutical, food and other industries.

Fifteen percent of the total world production of dyes is lost during the dyeing process and released in the textile effluents [1]. Dye effluents pose certain hazards and environmental problems. They are not only aesthetic pollutants, but coloration of water by the dyes may affect photochemical activities in aquatic systems by reducing light penetration [2]. It has been also reported that several commonly used dyes are carcinogenic and mutagenic for aquatic organisms [3]. Removal of textile dyes from wastewater is one of the several major environmental concern because they are difficult

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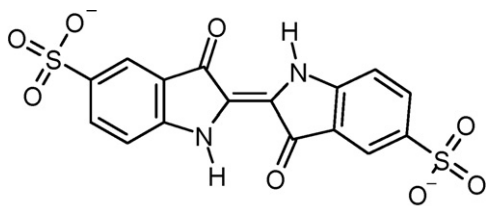


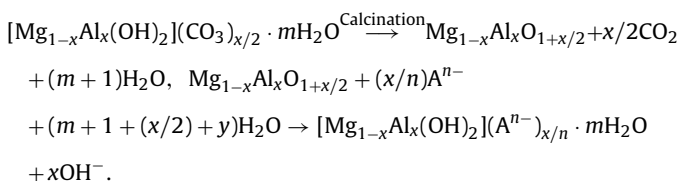
Fig. 1. Indigo carmine molecular structure.

to be removed by the conventional wastewater treatment systems (biological, physical and chemical methods) since they are designed to be resistant to degradation or fading by oxidizing agents and light. They must also be resistant to both high temperatures and enzyme degradation resulting from detergent washing. For these reasons, methods based on photo-degradation, aerobic and anaerobic biodegradation are slow and complete mineralization of most dyes is rather difficult. Degradation products are toxic to aquatic organisms [4]. Chemical and electrochemical oxidations, coagulation and reverse osmosis are generally not feasible on a large scale due to economic consideration. Adsorption, however, is an effective method for dye removal. In this way the application of layered double hydroxides (LDHs) and their calcined products (CLDHs) as adsorbents to selectively remove anionic pollutants from aqueous solutions have attracted considerable attention in the recent decade [5–10].

LDHs, also known as hydrotalcite-like compounds or anionic clays, are layered materials with hydroxide sheets, where a net positive charge is developed on the layer due to partial substitution of trivalent cations for divalent cations, balanced by exchangeable charge compensating anions and water molecules, which are present in the interlayer space [11]. They can be represented by the general formula [12].

$[M^{II}_x M^{III}_x (OH)_2] (A^{n-})_{x/n} \cdot mH_2O$ , abbreviated as  $[M^{II}-M^{III}-A]$ , where  $M^{II}$  is divalent cation like  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ , etc.,  $M^{III}$  trivalent cations like  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ , etc.,  $A^{n-}$  interlayer anion and  $x$  is defined as the  $M^{II}/(M^{II} + M^{III})$  ratio.

Calcined  $Mg-Al-CO_3$  LDHs 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 [6,11,13,14], as expressed by the following two equations [15]:



In the light of this so-called “memory effect” [13], the removal of indigo carmine (IC) (Fig. 1), a highly toxic indigoid class of dye from aqueous solution by calcined  $[Mg-Al-CO_3]$  was studied in this work. The effect of various factors such as pH of aqueous solutions, dye-adsorbent contact time, initial concentration of dye, and temperature of heating of LDHs have been investigated. The localization of the dye in the interlayer space and/or on external surfaces of the CLDHs is studied by X-ray diffraction (XRD), as well as by infrared spectroscopy (IR).

## 2. Materials and methods

### 2.1. Preparation of $[Mg-Al-CO_3]$

A solution containing  $Na_2CO_3$  (0.3 M) and NaOH (0.1 M) was added to 500 ml of distilled water until pH 10. Another solution containing a mixture of metal salts of  $Mg(SO_4)$ ,  $7H_2O$  and  $Al(Cl_3)$ ,  $6H_2O$  (total metal concentration 0.4 M, Mg/Al molar ratio 2:1) was prepared, and added dropwise to the pH 10 solution with continuous magnetic stirring. The pH was maintained constant by the simultaneous addition of the mixture of  $Na_2CO_3$ , NaOH. Once addition was completed, the slurry was magnetically stirred at room temperature for 72 h. The precipitate was filtered, washed several times with water and then dried at room temperature. CLDHs were obtained by heating LDHs at various temperatures: 300, 400, 500, 600 and 700 °C for 6 h.

### 2.2. Retention experiments

Retention experiments were carried out by the batch equilibrium technique at room temperature (20 °C), at constant pH, maintained by addition of NaOH and under a stream of  $N_2$  in order to avoid, or at least minimize, the contamination by atmospheric  $CO_2$ . Amounts of CLDHs were dispersed in 100 mL IC solutions. The initial concentration of IC was varied between 0.01 and 4 mmol  $L^{-1}$ . After filtration, the solid products obtained were dried at room temperature before being analysed by XRD and IR. The supernatants were recovered and the residual dye concentration was determined by UV-vis spectroscopy. The absorbance was measured at 610 nm on a SPECTRONIC GENESYS 5 spectrophotometer.

The quantity of IC, retained by the CLDHs,  $Q$ , was calculated as the difference between initial and equilibrium (final) concentrations of the dye in solution ( $C_i$  and  $C_e$ , 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 an XPERT-PRO diffractometer with  $Cu K\alpha$  radiation (45 kV and 40 mA). Measurement conditions were  $2\theta$  range: 2–76°, step size: 0.017°  $2\theta$ , step counting time: 41 s. Absorbance IR spectra were recorded on a Bruker Vertex 70 spectrophotometer, at a resolution of 4  $cm^{-1}$  and averaging over 20 scans, in the range 400–4000  $cm^{-1}$ . Samples were pressed into KBr disks.

## 3. Results and discussion

### 3.1. Characterization of $[Mg-Al-CO_3]$

#### 3.1.1. X-ray diffraction

Calcination of LDHs higher than 400 °C resulted in an almost complete decomposition of the  $LDH-CO_3^{2-}$ , evolving  $CO_2$  and water; consequently, a magnesium oxide was formed (Fig. 2). Miyata reported that on calcination of an  $LDH-CO_3^{2-}$  at less than 800 °C,  $Al^{3+}$  in the structure remains inside the formed  $MgO$ , resulting in a  $Mg-Al$  oxide solid product that is capable of being restored to a LDH when rehydrated [16]. However, when CLDHs was exposed to the air (adsorption of  $CO_2$  and humidity), the layered structure was reconstructed [17,18]. In our study, the CLDHs are reverted to the layered structure under humid atmospheric air and at room temperature (Fig. 3). However, upon reconstruction, the peaks become finer and intense when the temperature of calcination increases.

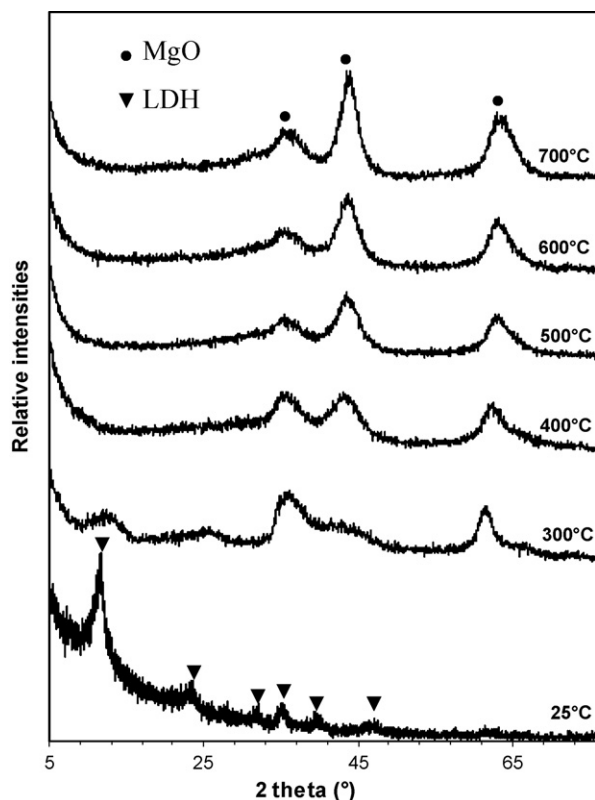


Fig. 2. XRD patterns of uncalcined Mg–Al–CO<sub>3</sub> LDH (25 °C), and Mg–Al–CO<sub>3</sub> LDH calcined at 300, 400, 500, 600 and 700 °C.

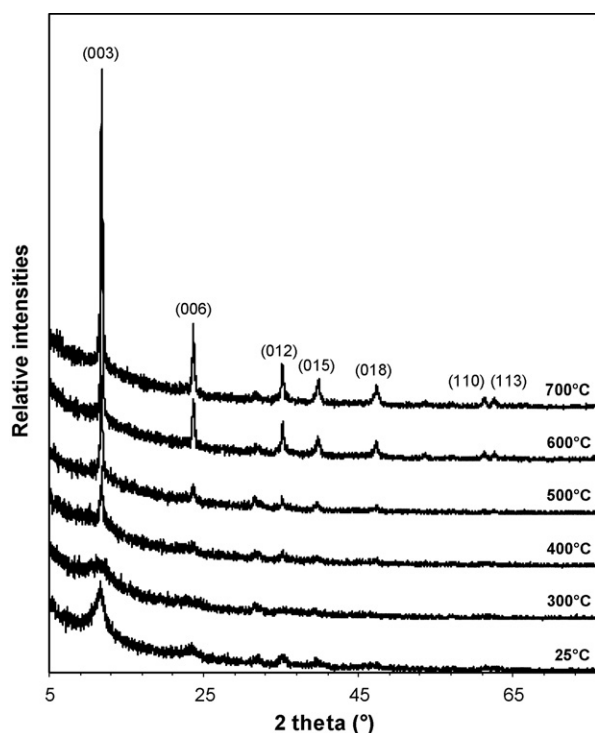


Fig. 3. X-ray diffraction patterns of LDH and rehydrated-CLDHs.

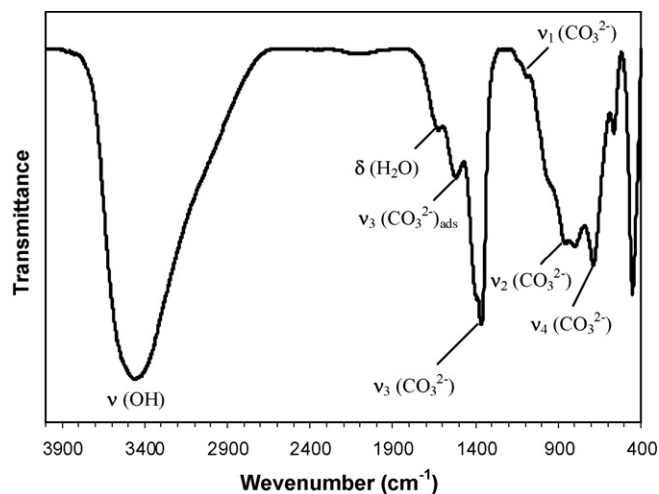


Fig. 4. IR spectra of [Mg–Al–CO<sub>3</sub>].

The XRD patterns exhibit the characteristic diffractions of well-crystallized hydroxalcite-like LDHs (ICSD collection code 086655) and no other crystalline phases are present. The (003) and (006) peaks are attributed to basal reflections, corresponding to successive stacking of the brucite-like sheets. The remainder peaks are attributed to non-basal reflections. The basal spacing ( $d_{003}$ ) of LDHs is 0.76 nm, which agrees well with values reported by other authors [14,19,20].

### 3.1.2. Infrared spectroscopy

The IR spectra of [Mg–Al–CO<sub>3</sub>] (Fig. 4) resemble those of other hydroxalcite-like phases [21,22]. Typical for these spectra are the strong broad absorbance bands between 3600 and 3200 cm<sup>-1</sup> associated with the stretching mode of hydrogen-bonded hydroxyl groups from both the hydroxide layers and interlayer water. A bending vibration band corresponding to a water deformation band,  $\delta(\text{H}_2\text{O})$ , is seen at 1630 cm<sup>-1</sup>. It can be seen also the presence of the IR active absorption bands arising from the carbonate anion observed at 1364–1390 ( $\nu_3$ ), 855 ( $\nu_2$ ) and 685 cm<sup>-1</sup> ( $\nu_4$ ). The two bands observed in the region 1360–1400 cm<sup>-1</sup>, can be attributed either to the disordered nature of the interlayer or to a lowering of the symmetry of the carbonate anions from D<sub>3h</sub> to C<sub>2v</sub> in the interlayer, which lifts the degeneracy of the  $\nu_3$  mode. The band of 1510 cm<sup>-1</sup> ( $\nu_3(\text{CO}_3^{2-})_{\text{ads}}$ ) and 1050 cm<sup>-1</sup> ( $\nu_1(\text{CO}_3^{2-})$ ) also suggests a lowering of the symmetry of the carbonate ion. These anions are related to a metal cation in substitution of ions hydroxyl of the layers. A series of bands are recorded at 450, 560, 799 and 940 cm<sup>-1</sup> ascribed to [AlO<sub>6</sub>]<sup>3-</sup> condensed groups, Mg/Al–OH translation, Al–OH translation and Al–OH deformation, respectively.

### 3.2. Effect of pH

Generally pH is considered to be an important parameter which controls the adsorption at water–adsorbent interfaces. Keeping this in view, the adsorption of IC (0.2 mmol/L) on CLDHs (20 mg) was studied at different pH values ranging from 5 to 9. Under these conditions, the dye adsorption on CLDHs is practically constant in the pH range studied (Fig. 5). Following these experiments, it was decided to carry out the retention experiments at pH of the solution (pH 8.8).

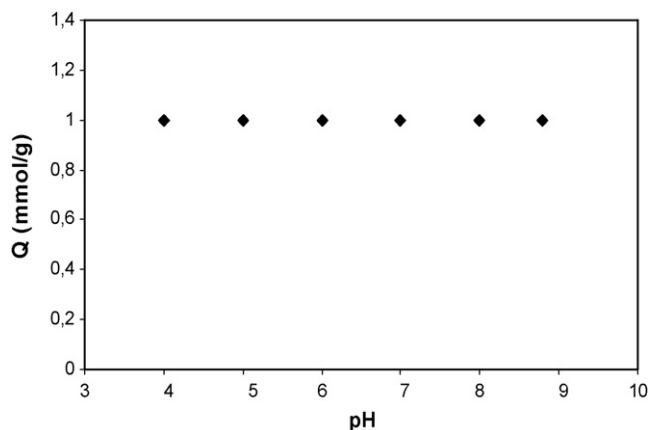


Fig. 5. Effect of pH on IC retention by CLDHs.

### 3.3. Effect of contact time

The amount of IC adsorbed by LDH calcined at 500 °C as a function of contact time, using a constant adsorbent mass of 20 mg and initial concentration of 0.2 mmol/L is shown in Fig. 6. The kinetic study shows that the adsorption equilibrium state is reached after a contact time of ~30–40 min since no change in the adsorbed amount is detected afterwards. To be sure that the equilibrium state is reached for higher concentrations, an IC–CLDHs contact time of 7 h was applied in the adsorption experiments.

### 3.4. Adsorption isotherms

The adsorption isotherms for IC sorption by CLDHs can be considered as L-type (Fig. 7), indicating that the interaction of sorbate–sorbent is much stronger than solvent–sorbent at the adsorption sites. The data obtained from the adsorption process was described by the Freundlich isotherm, which in linearized form is

$$\log Q = \log K + \frac{1}{n} \log C_e$$

where  $Q$  is the amount of dye per unit weight of the clay,  $C_e$  the equilibrium concentration of the adsorbate, while  $K$  and  $n$  are constants that estimate the adsorption capacity and intensity, respectively.

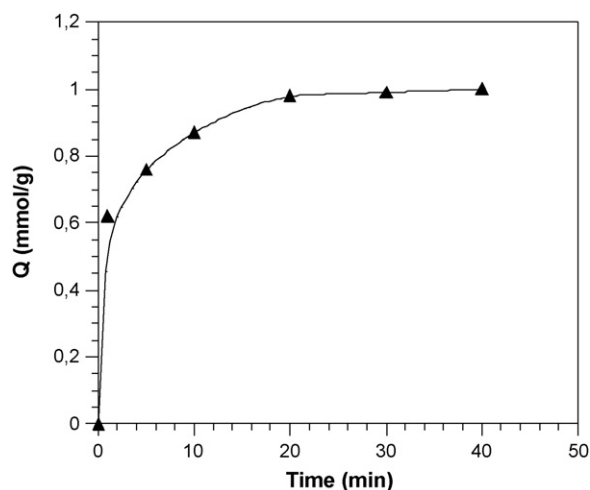


Fig. 6. Kinetics of IC (0.2 mmol/L) removal by 20 mg of the LDH calcined at 500 °C in 100 mL of solution.

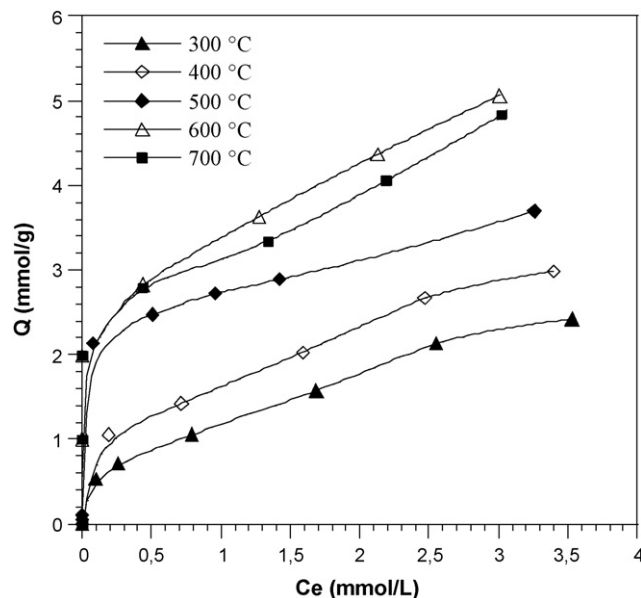


Fig. 7. Adsorption isotherms for IC determined with different CLDHs in 100 mL of solution.

The results of the fits are reported in Table 1. The  $1/n$  value in the range of 0,1–1 indicates a favourable adsorption process.

### 3.5. Mechanism of removal of IC

XRD patterns of the LDHs heated at 300, 400, 500, 600 and 700 °C obtained after retention of various quantities of IC are given in Fig. 8.

It is observed that the retention, for IC by LDHs heated at 300 and 400 °C, can be done by a weak intercalation of the IC noted by a new peak at weak  $2\theta$ . This weak retention, noted even for a great concentration in dye (4 mmol/L), can be justified by the presence of the ions carbonates not decomposed at temperatures 300 and 400 °C. Indeed, the interlayer carbonate of LDHs is decomposed completely when LDHs is calcined at 500 °C [13]. However, when the temperature of heating of LDHs is higher, the intercalation becomes significant and impacts the interlayer distance of the solids which increases from 0.76 nm in the initial phase [Mg–Al–CO<sub>3</sub>] to 2.13 nm in the new phase [Mg–Al–IC]. A light improvement of crystallinity is noted also when the IC concentration increases; indeed, the peaks become relatively more intense. The peak (1 1 0) towards 60° in  $2\theta$  is probably a sign of a light organization in the layers.

The results obtained by XRD was also confirmed by IR (Fig. 9), for the uptake of IC by LDHs heated at 300 and 400 °C it notes the presence of the band of carbonate at 1369 cm<sup>-1</sup>. The bands of  $\nu(\text{C}=\text{O})$  at 1641 and 1660 cm<sup>-1</sup> separately appear in IC spectra because of intramolecular hydrogen bonding between C=O and N–H [23]. After retention, the band at 1660 cm<sup>-1</sup> due to intramolecular hydrogen bonding disappears from the spectrum, whereas the band at 1641 cm<sup>-1</sup> becomes more intense probably by the forma-

Table 1  
Freundlich parameters for the retention of IC by different CLDHs in 100 mL of solution

Calcination temperature (°C)	1/n	K (mmol/g)	r <sup>2</sup>
300	0.48 ± 0.05	1.31 ± 0.07	0.977
400	0.42 ± 0.04	1.77 ± 0.07	0.989
500	0.15 ± 0.02	2.88 ± 0.07	0.990
600	0.14 ± 0.05	3.83 ± 0.28	0.905
700	0.13 ± 0.05	3.64 ± 0.3	0.882



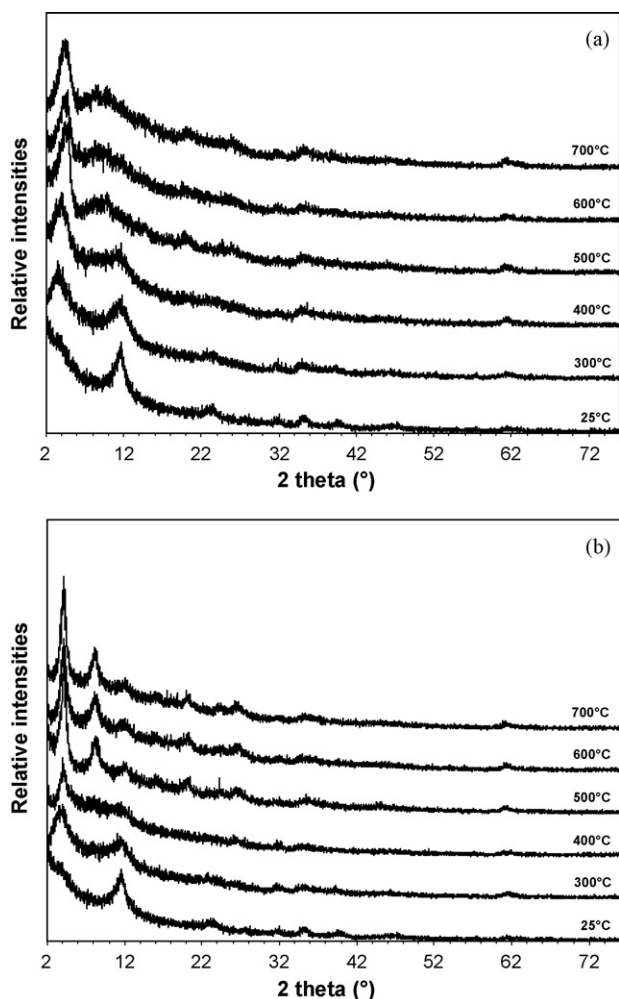


Fig. 8. XRD patterns of uncalcined Mg–Al–CO<sub>3</sub> LDH (25 °C) and the phases obtained after retention of IC by 20 mg of different CLDHs in 100 mL of solution at different IC initial concentrations (a) 0.4 mmol/L and (b) 4 mmol/L.

tion of intramolecular or intermolecular hydrogen bonding with N–H group.

The C–C single (681 cm<sup>-1</sup>), double bonding of the ethylenic (1615 cm<sup>-1</sup>) and double bonding of the aromatic ring system (1404, 1476 cm<sup>-1</sup>) are also present in the spectra [24].

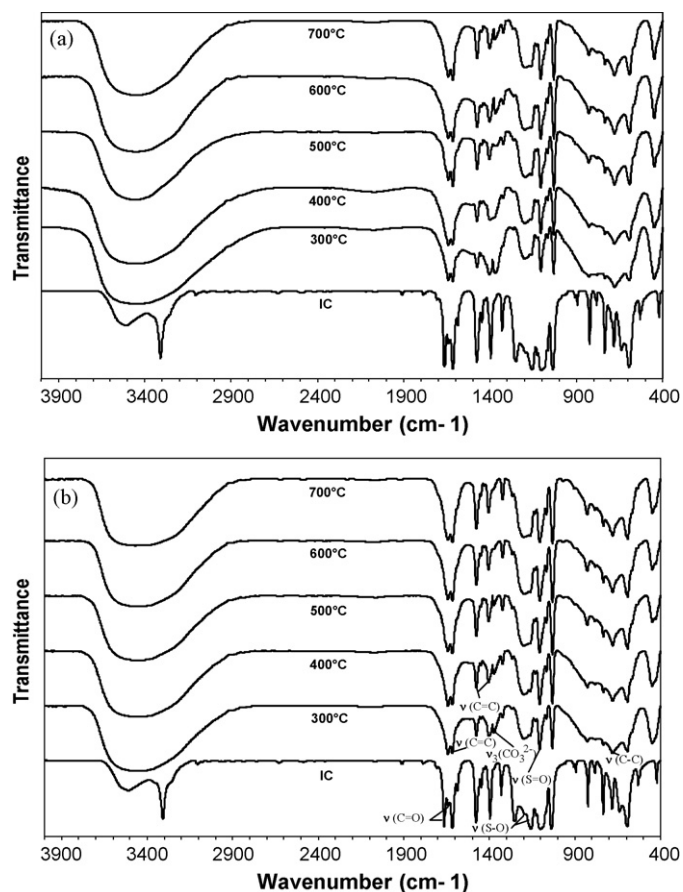


Fig. 9. IR spectra of IC and the phases obtained after retention of IC by 20 mg of different CLDHs in 100 mL of solution at different IC initial concentrations (a) 0.4 mmol/L and (b) 4 mmol/L.

The fixation of IC anions can be shown by the shift of the bands at 1155 and 1191 cm<sup>-1</sup> due to S–O bandings to 1162 and 1200 cm<sup>-1</sup> with a considerable decrease in intensity of the band at 1162 cm<sup>-1</sup> after retention. The band assigned to  $\nu(\text{S}=\text{O})$  at 1101 cm<sup>-1</sup> is also shifted to 1107 cm<sup>-1</sup> [23–28]. The displacement of these vibrations indicates that the uptake involved the sulfonate groups of the IC dye. Adsorption through sulfonate groups has already been observed in the case of adsorption of IC on TiO<sub>2</sub> [29].

In the light of these results, we can deduce that the adsorption of IC is enhanced by reconstruction of a matrix hydrocalcite inter-

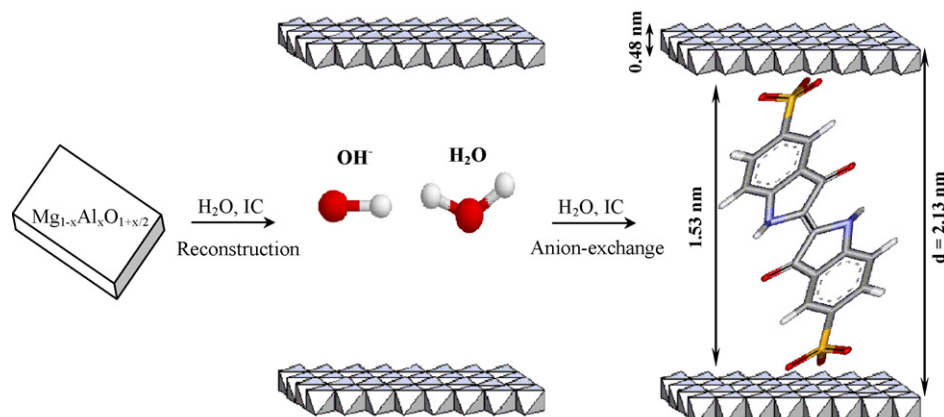


Fig. 10. The schematic illustration of IC intercalation between brucitic sheets.

caled by the dye bounding in the interlayer spaces by electrostatic interactions and hydrogen bonding. This process takes place by reconstruction of the oxide, with intercalation of hydroxyl anions, which are subsequently replaced by IC via an ion-exchange process [9,14]. Moreover, because of the extreme positions of the sulfonate groups, the flat indigo carmine molecule may be indicates a perpendicularly orientation in the host matrix with an interlayer distance of 2.13 nm [28–30]. Knowing the thickness of the LDHs layer is 0.48 nm, gives the gallery height of  $[\text{Mg-Al-CO}_3]$  after retention as 1.65 nm. The value of long axis of IC anion (1.53 nm), calculated from the semi-empirical molecular orbital method of Gaussian 03 software, is well consisted with the gallery height of  $[\text{Mg-Al-CO}_3]$  after the uptake of IC anion, as shown in Fig. 10.

#### 4. Conclusion

From the present study, it can be seen that the CLDHs can be used effectively for the removal of the IC dye from aqueous solutions. The quantity eliminated was found to depend on the calcination temperature from LDHs, the initial concentration of the dye and the dye-adsorbent contact time but does not depend on the pH of the solution. The adsorption is described by Freundlich-type isotherm for all adsorbent due to the surface in homogeneity. The removal of the dye from aqueous solutions is induced by adsorption on surface sites of the CLDHs and a weak intercalation of the dye into LDHs heated at 300 and 400 °C justified by the presence of the ions carbonates not decomposed at these temperatures. The intercalation of the organic anion in the layered host structure was clearly evidenced for matrix heated higher than 400 °C and reconstructed in the presence of high concentration of dye (4 mmol/L). In this case the net increase in the basal spacing from 0.76 nm for  $[\text{Mg-Al-CO}_3]$  to 2.13 nm for the organic derivative. We can also deduce that the adsorption of IC is enhanced by reconstruction of a matrix hydrotalcite intercalated by the dye bounding in the interlayer spaces by electrostatic interactions and hydrogen bonding.

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