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Removal of methyl orange dye from water to zinc-aluminium-chloride layered double hydroxides

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Layered double hydroxides (LDHs) or hydrotalcite-like compounds with Zn and Al in the layers and chloride in the interlayer, was prepared following the coprecipitation method at constant pH. The affinity of this material with a hazardous dye Methyl Orange (MO) was studied as a function of contact time, initial pH of the solutions and initial dye concentration. It was found that 8h is enough time for the equilibrium state to be reached in OM adsorption. OM removal was independent of the initial pH. The adsorption isotherm, described by the Langmuir model, are of L-type. The results, demonstrate that the MO adsorption on LDHs occurs by both adsorption on external surface and interlayer ion exchange. A mechanism for removal of MO anion has been confirmed by X-ray diffraction and IR spectroscopy.

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Keywords: Layered double hydroxides, Methyl Orange, Dye, Adsorption, Anion exchange

1. Introduction

The treatment of waste water from textile and dyestuff Moroccan industries is one of the most challenging. These effluents pose certain hazards and environmental problems. They are not only aesthetic pollutants, but colouration of water by the dyes may affect photochemical activities in aquatic systems by reducing light penetration [1]. It has been also reported that several commonly used dyes are carcinogenic and mutagenic for aquatic organisms [2]. For example Methyl Orange, water-soluble azo dye, on inadvertently entering the body through ingestion, metabolized by intestinal microorganisms into aromatic amines. Reductive enzymes in the liver can also catalyse de reductive cleavage of the azo linkage to produce aromatic amines and can even lead to intestinal cancer [3,4]. The toxic nature of the dye is still not quantified much but its high content in living systems can prove to be harmful. In order to solve this problem, adsorption techniques appear as an efficient way to remove coloured contaminants especially when they are non-biodegradable. Among the different adsorbents, the Layered double hydroxides (LDHs), also known as hydrotalcite-like-compounds or anionic clays, are promising waste carriers, particularly for dye molecules [5,6]. Owing to both high anionic exchange capacities and high layer charge densities, they favour strong interactions with anionic pollutants. These materials possess a layered structure of general formula [5]:

$[M^{II}_{1-x} M^{III}_{x} (OH)_2](A^{n-})_{x/n} . mH_2O$, 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.

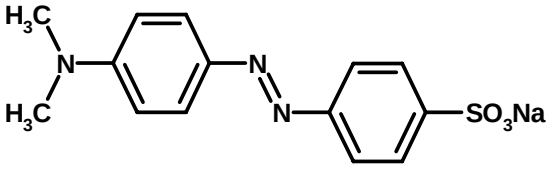

Fig. 1. Methyl orange molecular structure

The aim of the present work is to assess the sorption capacity of the dye Methyl Orange (MO) (Fig.1) on [Zn-Al-Cl] LDHs and to understand the mechanisms. The influence of contact time, initial pH of the solutions and initial dye concentration have been investigated. The localization of the dye in the interlayer space and/or on external surfaces of the LDHs is studied by X-ray diffraction (XRD), as well as by infrared spectroscopy (IR) and discussed from the determination of the apparent interlayer spacing of the LDHs.

2. Materials and methods

2.1. Preparation of [Zn_2-Al-Cl]

The experiment was carried out under a stream of N_2 in order to avoid, or at least minimise contamination by atmospheric CO_2. The anionic clay [Zn-Al-Cl], with a [Zn]/[Al] ratio equal to 2, was synthesised by coprecipitation at a constant pH of 9.0. Mixtures of molar $ZnCl_2$ and $AlCl_3$ aqueous solutions were slowly introduced into the reactor where the pH was maintained by the simultaneous addition of 1.0 M NaOH solution. The resulting slurry was then left under stirring for 34 h at

room temperature. The precipitate was filtered and washed several times with water and then dried at 30 °C.

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. Amounts of [Zn-Al-Cl] were dispersed in 100 mL MO solutions. The initial concentration of MO was varied between 0.015 and 1.5 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 464 nm on a SPECTRONIC GENESYS 5 spectrophotometer.

The quantity of MO retained by [Zn-Al-Cl], 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:

$$Q = (C_i - C_e)V/m \quad (1)$$

2.3. Structural characterization techniques

The XRD equipment used was a XPERT-PRO diffractometer with Cu K_α radiation (45 kV and 40 mA). Measurement conditions were: 2θ range: 2-76°, step size: 0.017° 2θ, step counting time: 41s. 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.

For SEM a Philips scanning electron microscope was utilized. The accelerating voltage was 25 kV.

3. Results and discussion

3.1. Characterisation of [Zn-Al-Cl]

3.1.1. X-ray diffraction

The XRD pattern for [Zn-Al-Cl] (Fig. 2), which shows good agreement with those found for other hydrotalcite-like compounds [7], indicates that the solid consists of a well crystallised single phase with large crystallites. The lattice parameters were refined on the hexagonal lattice with a rhombohedral symmetry (space group: R-3m), are: a = 0.31 nm and c = 2.33 nm (d = c/3 = 0.78 nm).

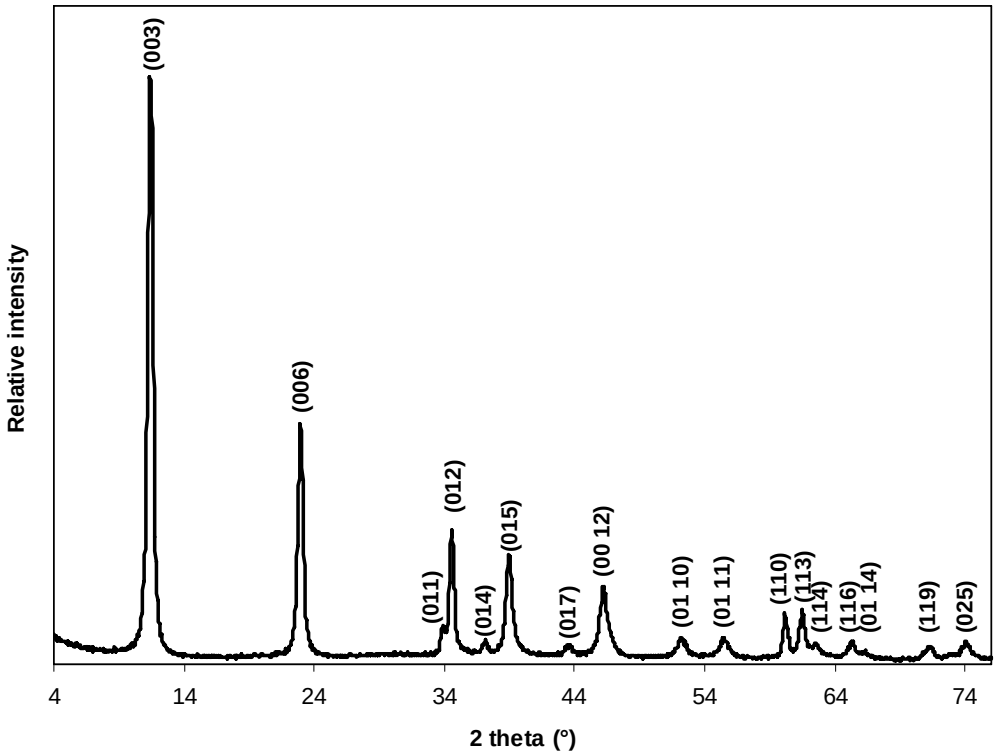

Fig. 2. XRD pattern of [Zn-Al-Cl].

3.1.2. Infrared spectroscopy

The IR spectrum of the sample (Fig. 3) presents profiles which resemble those exhibited by all hydrotalcite-like phases [7]. Typical of this spectrum are the strong absorbance at 3450 cm^{-1} and the band at 1650 cm^{-1} which correspond to the valence vibrations of hydroxyl groups and the bending vibration of water, $\delta(H_2O)$, respectively. The bands observed in the low frequency region of the spectrum correspond to the lattice vibration modes and can be attributed to M-O (841 and 647 cm^{-1}) and O-M-O (435 cm^{-1}) vibrations [8,9]. It is noted that, despite the precautions taken during the materials syntheses, the IR spectrum shows some contamination by CO_3^{2-} (1360 cm^{-1}) in the solid. However, CO_3^{2-}, which is known to form stable anionic clays [10], is only present in trace amounts, since no carbonate clay phase is visible in the XRD pattern (Fig. 2).

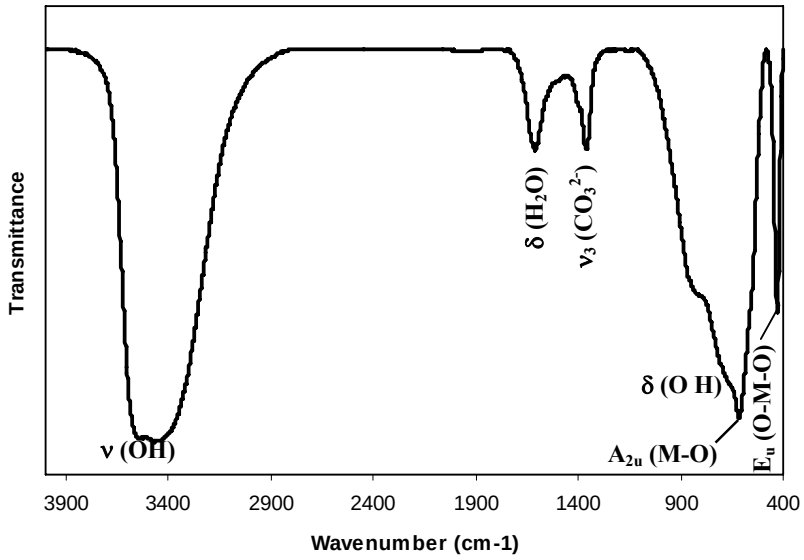

Fig. 3. IR spectrum of [Zn-Al-Cl].

3.1.3. Scanning electron microscopy

The SEM image of [Zn-Al-Cl] reported in Fig. 4, shows aggregates composed of crystallites probably resulting from the superposition of layers. This layered character of the compound is proof of a good crystalline organization.

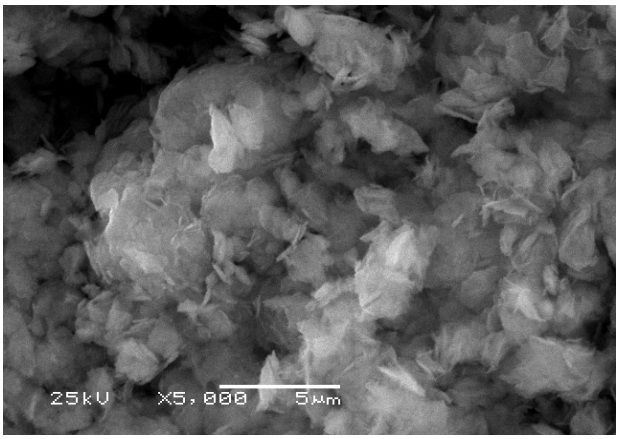

Fig. 4. Scanning electron micrographs of [Zn-Al-Cl]

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 MO (0.15 mmol/L) on [Zn-Al-Cl] (20 mg) was studied at different pH values ranging from 4 to 9. Under these conditions, the dye adsorption on LDHs 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=7).

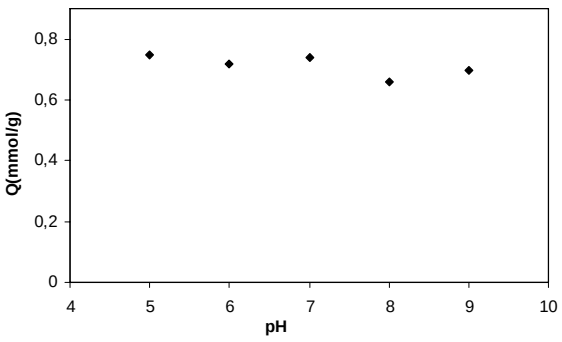

Fig. 5. Effect of pH on MO retention by [Zn-Al-Cl]

3.3. Effect of contact time

The amount of MO adsorbed by [Zn-Al-Cl] as a function of contact time, using a constant adsorbent mass of 20 mg and initial concentration of 0.15 mmol/L, is shown in Fig. 6. The kinetic study shows that the adsorption equilibrium state is reached after a contact time of 40 min since no change in the adsorbed amount is detected afterwards. To be sure that the equilibrium state is reached for higher concentrations, a MO-LDHs contact time of 8h was applied in the adsorption experiments.

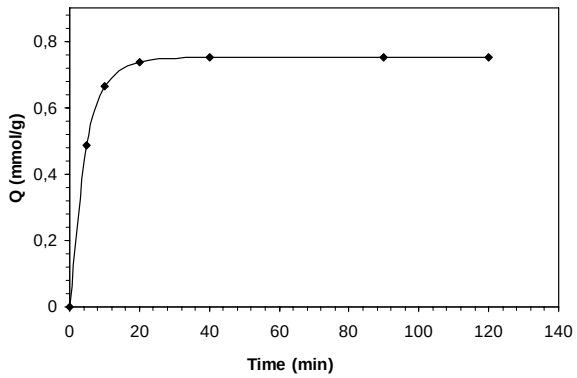

Fig. 6. Kineties of MO (0.15 mmol/L) removal by 20 mg of [Zn-Al-Cl] in 100 mL of solution.

3.4. Adsorption isotherms

The dye adsorption isotherm on [Zn-Al-Cl] can be considered clearly as pure L-type (Fig.7), indicating that the interaction sorbate-sorbent is much stronger than solvent-sorbent at the adsorption sites. Isotherm with this profile are typical of systems where the monofunctional adsorbate is strongly attracted by the adsorbent, mostly by ion-ion interaction, reaching a saturation value given by the isotherm plateau. These results again suggest that MO anions are preferentially removed. In this case, adsorption isotherm is described by Langmuir isotherm, which in linearized form is:

$$C_e / Q = C_e / Q_m + 1 / KQ_m \quad (2)$$

where C_e is the equilibrium concentration of the dye, Q is the quantity of MO adsorbed per gram of the LDHs, Q_m is the maximum amount adsorbed per unit mass of LDHs and K is the affinity constant (Fig.8).

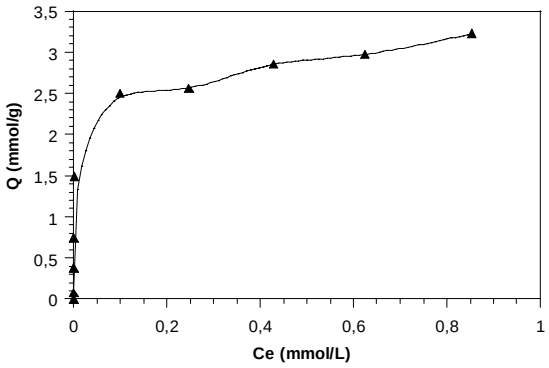

Fig. 7. Adsorption isotherm for MO determined with 20mg of [Zn-Al-Cl] in 100mL of solution

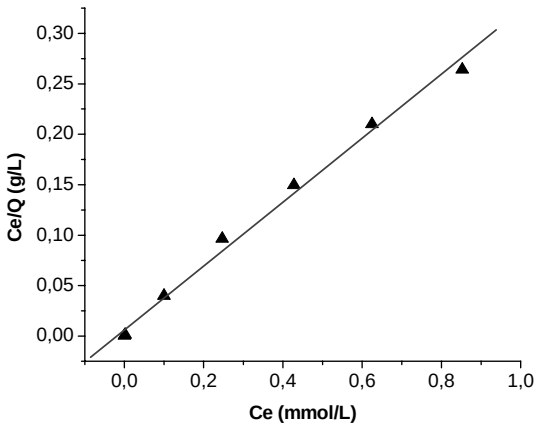

Fig. 8. Langmuir adsorption isotherm of MO on [Zn-Al-Cl] (Langmuir adsorption constants: Q_m =3.155 mmol/g, K = 53.272 and R^2 = 0.997).

3.5. Mechanism of removal of MO

XRD patterns of the LDHs obtained after retention of various quantities of MO (Fig. 9) indicates that the best extent of ion exchange is obtained for the concentration 1.5 mmol/L. Below this concentration (0.3 mmol/L), the XRD patterns present some lines corresponding to the chloride phase. The intercalation of the organic anion in the layered host structure is clearly evidenced by the net increase in the basal spacing from 0.78 nm for [Zn-Al-Cl] to 2.4 nm in the new phase [Zn-Al-MO]. The intercalation is also confirmed by IR (Fig. 10). All stretching and bending vibration modes of the organic anion are observed in the spectrum.

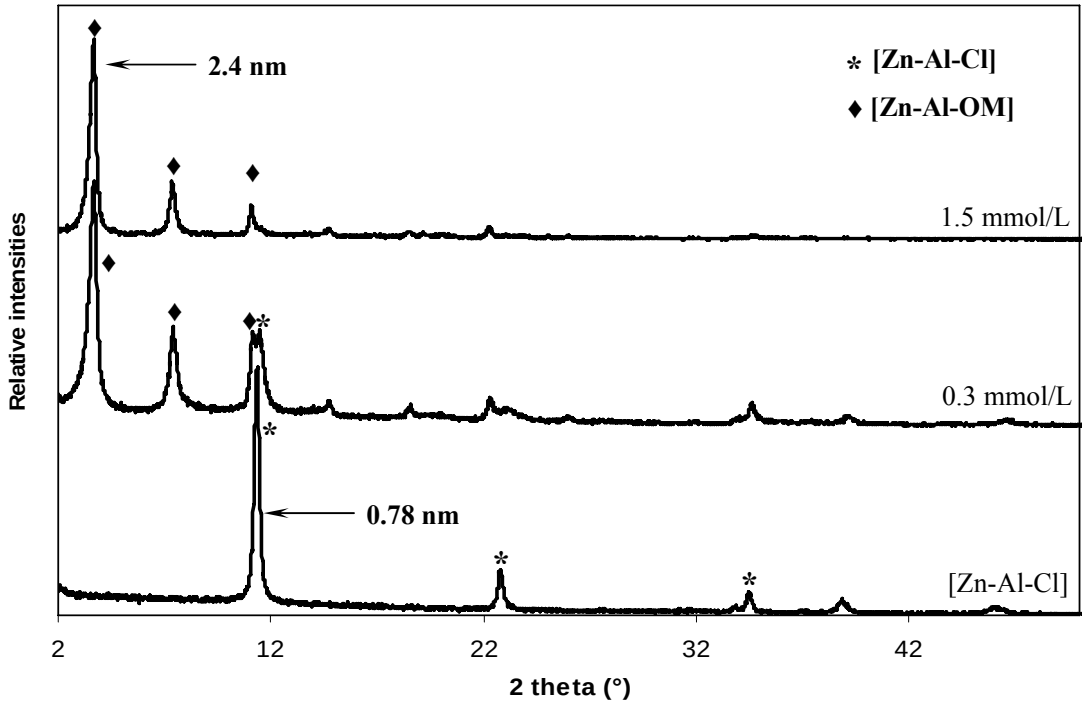

Fig. 9. XRD patterns of [Zn-Al-Cl] and the phases obtained after retention of MO by 20 mg of [Zn-Al-Cl] in 100 mL of solution at different MO initial concentrations.

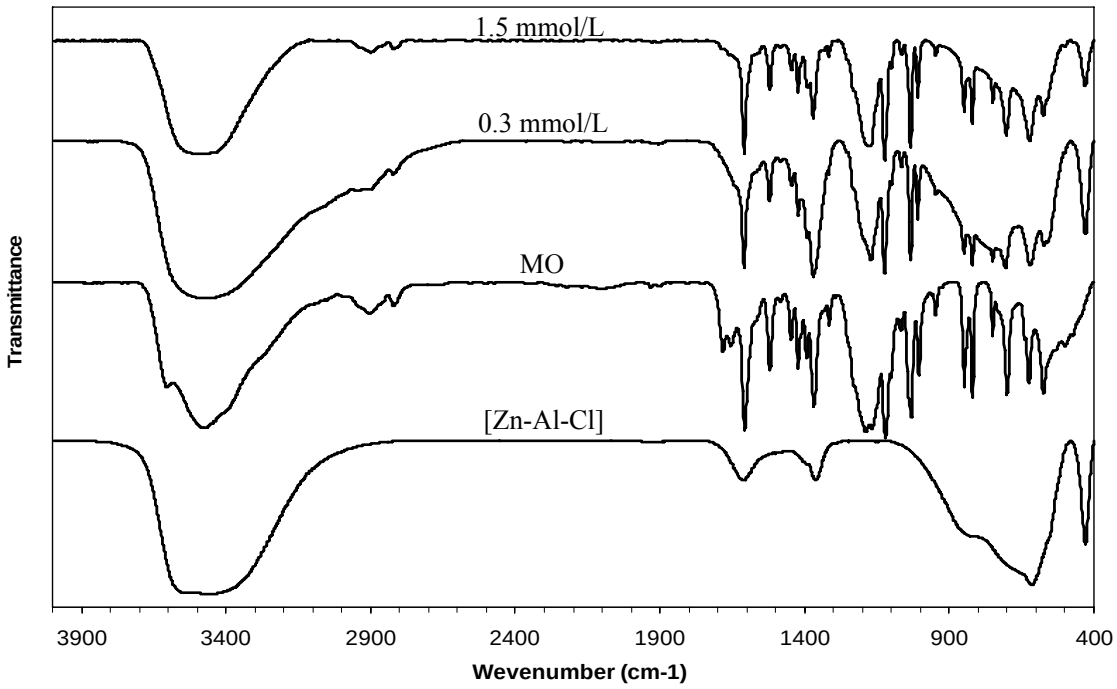

Fig. 10. IR spectra of [Zn-Al-Cl], MO and the phases obtained after retention of MO by 20 mg of [Zn-Al-Cl] in 100 mL of solution at different MO initial concentrations.

In the light of these results, we can deduce that the MO anion is intercalated in the interlayer space and bound to the host matrix by electrostatic interactions and hydrogen bonding with an interlayer distance of 2.4 nm. Knowing the thickness of the brucite-like layer (0.21 nm) and the hydrogen bond distances between guest and host (0.27 nm) suggests that the gallery height is close to 1.65 nm. The length of MO anion of 1.32 nm [6] may be associated with an opposite and perpendicular orientation for the anion, with anionic functions attached to the hydroxylated lattice through strong hydrogen bonding and electrostatic attraction between MO anion and positively charged lattice of LDH. Fig. 11 presents a schematic diagram of the arrangement of MO anion in the new phase [Zn-Al-MO]. Previous intercalation results in LDH-like materials have shown the propensity of this class of layered materials to incorporate organic anions in a perpendicular arrangement [11,12,13].

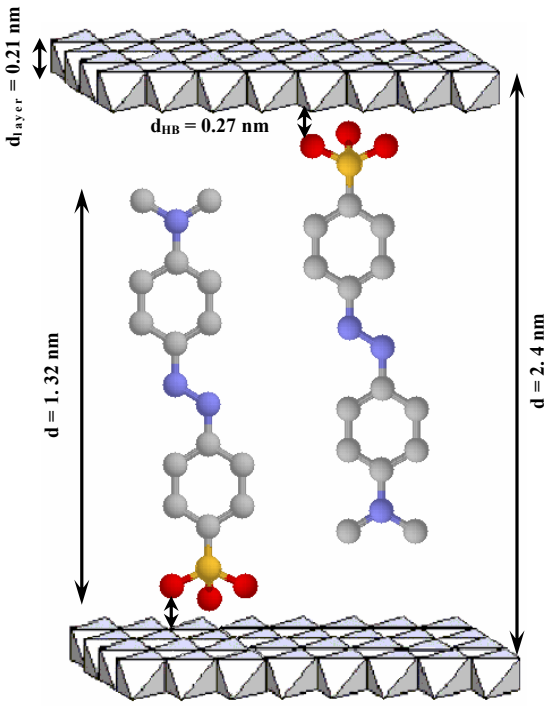

Fig. 11. The schematic illustration of MO intercalation between brucitic sheets.

4. Conclusion

The present study, shows that the [Zn-Al-Cl] can be used as an effective adsorbent for the removal of the MO dye from aqueous solutions. The quantity eliminated was found to depend on 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 Langmuir -type isotherm due to the surface homogeneity. The removal of the dye from aqueous solutions is induced by both adsorption and internal exchange. The intercalation of the organic ion in the layered host structure was clearly evidenced by the net increase in the basal spacing from 0.7802 nm for [Zn-Al-Cl] to 2.3958 nm in the new phase, [Zn-Al-MO]. This intercalation was also confirmed by IR, with all stretching and bending vibration modes of the organic anion being present on the spectra, besides the absorption bands of the hydroxylated layers.

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