

## Removal of organiques pollutants using anionique clays.

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**Abstract** -- Hydrotalcite (HT) or hydrotalcite-like compounds (HTlc) are layered double hydroxides belonging to the class of anionic clays. The structure of these compounds are very similar to that of brucite, Mg(OH)<sub>2</sub>, where some of Mg<sup>2+</sup> represented as [M<sup>(II)</sup>] are isomorphously replaced by Al<sup>3+</sup> represented as [M<sup>(III)</sup>] and the net positive charge is compensated by the inter-layered exchangeable anion (A<sup>n-</sup>).

LDH has been receiving increasing attention in recent years, owing to its potential technological applications such as catalysis, electrode, optical memory, separator, adsorbent, precursor for composite materials, and ion exchange.

The general formula of these compounds can be represented as:

$[M^{(II)}_{1-x}M^{(III)}_x(OH)_2] \cdot A^{n-}_{x/n} \cdot mH_2O$  with M<sup>(II)</sup> and M<sup>(III)</sup> as metal cations and A<sup>n-</sup> as exchangeable anion.

LDHs also possess relatively large surface areas and high anion-exchange capacities. Because of these properties, LDHs have been studied for removing toxic anionic species from aqueous systems.

Thermal decomposition of these materials by calcination above 420°C results in the formation of high surface area basic mixed oxides which are reported to be potential candidates in catalyzing various reactions involved in the synthesis of a variety of fine chemicals.

Indeed at this temperature, the as formed mixed oxides solid solution can regenerate upon rehydration the HT structure with the suitable anions present in solution. Therefore, this so-called reconstruction process may be used to improve the sorption of anionic species.

The LDHs has been synthesized by the coprecipitation method at pH constant. The material has been obtained with [Mn/Al] molar ratio of 2.0.

The product is characterized by X-ray diffraction (XRD), spectroscopy infra red (FTIR), and differential thermal analysis/thermo gravimetric analysis (DTA/TG). Dosages of polluted solutions have been realized by spectrometry UV visible.

**Key words:** LDH, adsorption, catalysis, FTIR, DRX.

### 1. INTRODUCTION

The effluent discharged by various textile, paper or plastic industries contains a large number of dyes, increasing the total chemical oxygen demand (COD) of wastewaters [1]. Although most of the dyes are non-toxic, many of them bound to highly toxic metals (e.g. Cr) with harmful consequences to the aquatic life in rivers. Moreover, the persistence of colour appearance (at concentration above 1 mg/L) in treated wastewaters prevents their re-use. Because of stringent government legislations, several methods [2] are used for their decolourisation such as bio-chemical or photo-degradation. Adsorption techniques appear also as an efficient way to remove coloured contaminants especially when they are nonbiodegradable.

Among the different adsorbents, the anionic clays [3], are promising waste carriers [4], particularly for dye molecules [5]. Owing to both high anionic exchange capacities and high layer charge densities, they favor strong interactions with anionic pollutants.

These materials possess a layered structure of general formula:  $[M^{(II)}_{1-x}M^{(III)}_x(OH)_2] A^{n-}_{x/n} \cdot mH_2O$  that can be described by comparison to the brucite-like structure, M<sup>(II)</sup>(OH)<sub>2</sub>. The positive charge of the layers created by the substitution of part of the divalent cations by trivalent cations is compensated by the presence of anions in the interlayer spaces. Hydrotalcite (HT), the natural occurring mineral

$Mg_6Al_2(OH)_{16}(CO_3^2-)_4H_2O$ , is the most representative member of the HT-like compounds or LDH family.

Hydrotalcites can be synthesized through several precipitation methods [6]. Co precipitation is the usual procedure, it is a time consuming technique, which requires large volumes of water. This method in the presence of microwave irradiation, not only reduces preparation time, but it provides original materials. The MgAl matrix displays the strongest affinity for the carbonate anions, which cannot be readily exchanged by other anions, limiting their use as sorbent for anionic pollutants. Nevertheless, one interesting way to replace the carbonate anions consists in heating the HT at a temperature of 450 °C. Indeed at this temperature, the as formed mixed oxides solid solution can regenerate upon rehydration the HT structure with the suitable anions present in solution. Therefore, this so-called reconstruction process may be used to improve the sorption of anionic species.

## 2. EXPERIMENTAL SECTION

### 2.1. Hydrotalcites preparation

The Mn-Al HT with a  $Mn^{+2}/Al^{+3}$  molar ratio of 2/1 was synthesized by coprecipitation [7]. Two aqueous solutions, one containing both  $Mn(NO_3)_2$  from Aldrich, 98% and  $Al(NO_3)_3$  from Aldrich, 99%, hydrated salts, and the other NaOH (1.85 M) from Baker, 98%, were added dropwise into a flask at room temperature. The pH was maintained between 7.5 and 8.5 [8,9]. After precipitation, samples were irradiated in a microwave oven (MIC-I, Sistemas y Equipos de Vidrio, S. A. de C. V.) operating at 200 W for 10 min to accelerate condensation and crystallization steps [10]. The maximal temperature reached into the reactor was 353 K. The mixture final volume was about 400 ml to obtain 20 g of dried product. Prior to drying at 343 K for 24 h, the precipitates were washed with deionized water.

The Mn-Al sample turned out to be brown. An intense brown color was the feature of the dried product. The hydrotalcite like compound was calcined at 523 and 693 K in a muffle for 6 h.

### 2.2. Characterization

X-ray diffraction (XRD) patterns were recorded with a Bruker axs D8 advance diffractometer coupled to a copper anode X-ray tube.

Thermal analyses, including thermogravimetry (TG) and differential thermal analysis (DTA), were carried out using a Netzsch STA 409 instrument. The heating rate of 50°C min<sup>-1</sup> in air or argon with 50 mg of sample was used.

A PerkinElmer GX series spectrometer in a wavenumber interval of 4000-400 cm<sup>-1</sup> was used to measure the FTIR spectra.

## 2. RESULTS:

### 2.1. Dried samples

#### 2.1.1. X-ray diffraction

The XRD pattern of the HT dried at 343 K is shown in Fig. 1. It corresponds to a hydrotalcite-like structure; the average  $d_{003}$  distance is 7.74Å° for the sample; the  $d_{003}$  distance is similar to the often reported value in HTs [11].

The brown color of the Mn samples has to be attributed to the oxidation process:  $Mn^{(II)}$  to  $Mn^{(IV)}$ . Indeed,  $Mn^{(II)}$  cations in an octahedral OH environment are slightly pink (as hexa aqueous manganese(II) cations).

Besides, parameters  $a$  and  $c$ , displayed in Table.1, are consistent with a hexagonal unit cell; they were obtained from the hydrotalcite (110) and (003) reflections, respectively.

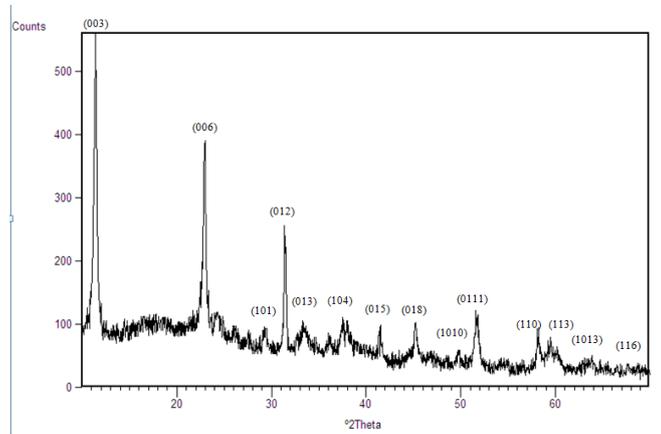


Figure.1. Powder XRD patterns of Mn-Al-CO<sub>3</sub> LDH

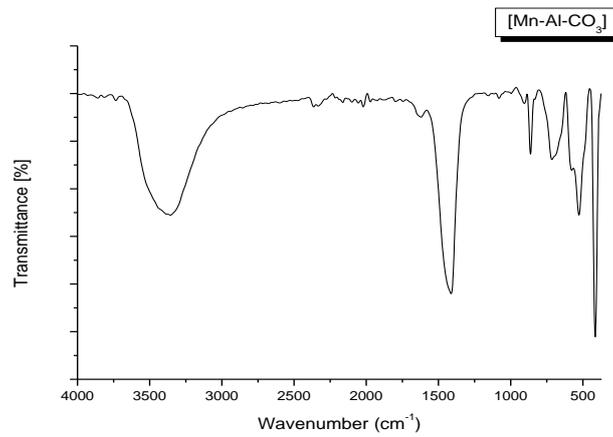


Figure.2. FTIR spectra of [Mn-Al-CO<sub>3</sub>] HT.

<b>Mn-Al-CO<sub>3</sub></b>	<b>d<sub>(003)</sub></b> (Å)	<b>d<sub>(006)</sub></b> (Å)	<b>d<sub>(110)</sub></b> (Å)	<b>c(Å)</b>	<b>a(Å)</b>
R=2	7.74	3.87	1.58	23.25	3,16

Tableau 1: LATTICE PARAMETERS FOR [MN-AL-CO<sub>3</sub>].

### 2.1.2. FTIR spectroscopy

The FTIR spectra are compared in Fig.2. All spectra present a broad adsorption band at  $3400\text{ cm}^{-1}$  attributed to the stretching vibration of the hydroxyl group (OH) from the hydroxide layers and the interlayer water. The broadening of this band is caused by the hydrogen bond formation [12,13]. The band close to  $1600\text{ cm}^{-1}$  corresponds to a deformation mode of  $\text{H}_2\text{O}$  molecules.

The vibration band at  $1500\text{ cm}^{-1}$  is assigned to the vibration mode of free carbonates. It can be observed for these phases, the appearance of another band around  $1350\text{ cm}^{-1}$ , attributed to the presence of carbonates. Vibration bands at low frequencies (below  $1000\text{ cm}^{-1}$ ) are assigned to the metal-oxygen bonds forming the metal layers laminated to each material. Bands observed below  $800\text{ cm}^{-1}$  are due to the vibration of the metal-oxygen bonds in the brucite-like sheets.

### 2.2.3. TGA experiments

Each thermogram has several well-differentiated mass loss as usually reported in the literature [14-19]:

- The first mass loss that occurs at a temperature below  $240\text{ °C}$  corresponds to the loss of physisorbed water on the surface of the material.
- Heating the samples at temperatures around  $370\text{ °C}$  leads to the loss of water molecules located in the area interlamellar.
- A third mass loss was recorded at about  $550\text{ °C}$  is associated with the decomposition of hydroxyl and carbonate anions to that of compensation ( $\text{CO}_2$  formation).

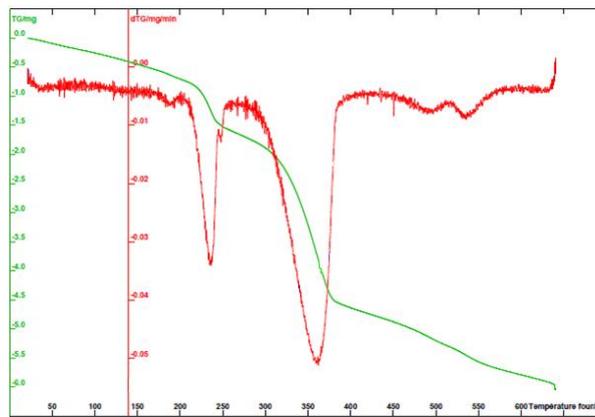


Figure.3. DTA/TG analysis for the sample  $[\text{Mn-Al-CO}_3]$ .

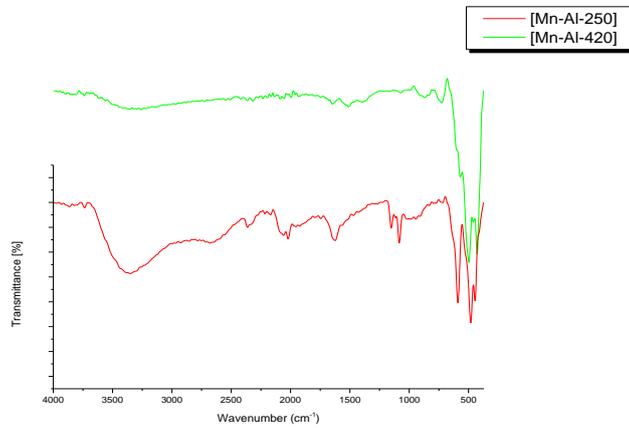


Figure 6. FTIR spectra of [Mn-Al] HT calcined at 250 and 420°C [Mn-Al-T(°C)]

### 2.3. Calcined samples

#### 2.3.1. X-ray diffraction

The diffractogram of phase [Mn-Al] calcined at 250 °C (Fig.4) reveals the almost complete transformation of the crystalline phase in an amorphous phase but with the beginning of a beginning, shy, training of an oxide which is likely to oxide of the spinel phase.

When the phase is calcined at 420 °C (Fig.5), the amorphous phase persists but however you can clearly see the emergence of a new oxide identified as the spinel structure.

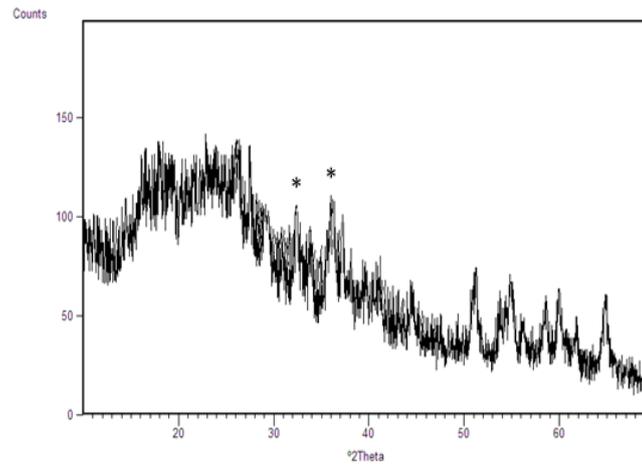


Figure 4. Powder XRD patterns of [Mn-Al-250]  
\*: Early appearance of the spinel phase

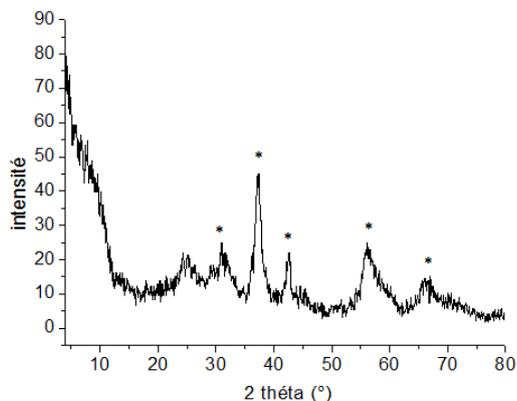


Figure.5. Powder XRD patterns of [Mn-Al-420]  
\*: Spinel structure

### 2.3.2. FTIR spectroscopy

The infrared spectra of calcined materials (Fig.6) show the relative decrease in the intensity of characteristic absorption bands of water molecules (about  $3400\text{ cm}^{-1}$  for [Mn-Al-250] and [Mn-Al-420]), and in the range  $700\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$  increases vibration of those corresponding link characteristics MO. We also observed that the band at around  $1370\text{ cm}^{-1}$  for both materials is still detectable. However, the low intensity of this band compared to that observed for the starting materials, suggests that carbonate ions are adsorbed on the surface of the grains of calcined materials, the presence of the carbonate ions may be due to contamination by carbon dioxide air [20,12].

## 3. CONCLUSION

This work has allowed us to get to know synthesized by coprecipitation a new range of materials: layered double hydroxides.

Different analysis techniques have confirmed that the synthesized solid correspond to the layered double hydroxides wanted

The series of Mn-Al mixed oxide based catalysts prepared by calcination of layered double hydroxides with  $M^{II}/M^{III}$  molar ratio of two were characterized by various methods.

The spinel structures were identified in all samples by X-ray diffraction and infrared spectroscopy.

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