

Comparative Study of Different Protocols for the Preparation of Anionic Clay-Polymer Nanocomposite (Hydrotalcite-Cellulose) and their Structural Properties

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ABSTRACT: In this study, different synthesis methods of nanocomposites, based on microcrystalline cellulose MCC and Hydrotalcite (family of layered double hydroxide LDH), were developed. The Hydrotalcite was previously prepared by a coprecipitation method. Four processes have been explored for synthesis of cellulose-Hydrotalcite nanocomposite: (I) Activation by microwave to the mixture of LDH dispersed in the cellulose solution (cellulose dissolved in 7%wt NaOH/12%wt urea aqueous solution). (II) The second method enables the synthesis of nanocomposite by the coprecipitation method which comprises adding drop wise a solution of magnesium-aluminium salts and carbonates solution to cellulose solution. (III) The third process consists in swelling the LDH and cellulose with distilled water and activating the mixture by microwave. (IV) The fourth protocol consists of the dispersion of cellulose in LDH-solution which was homogenized by ultrasonic radiation.

The influence of the reaction parameters including the synthesis methods and the structure of the composite obtained were discussed by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier Transform Infrared (FTIR) spectrometry. X-Ray diffraction (XRD) analysis and transmission electron microscopy (TEM) revealed the existence of partially exfoliated structure or mixed phase clay-cellulose. Analysis of Fourier Transform Infrared (FTIR) showed functional groups of cellulose and LDH with some differences.

Methods and conditions of processing were thoroughly investigated to obtain exfoliated and/or dispersed cellulose/LDH nanocomposites.

KEYWORDS: Layered Double Hydroxide, Hydrotalcite, Cellulose, Nanocomposites.

I. INTRODUCTION

Recently, composites derived from natural organic materials have received considerable attention due to their properties: easy processability, renewable origin, possibility of recycling [1] and good mechanical resistance [2]. Furthermore, an improvement in flame retardancy was also observed by Guolin Song et al. [3]. Biopolymer-clay nanocomposites are a new class of materials, they are prepared by addition of low amounts of clay to the biopolymer matrix [4].

Cellulose is the most abundant biomass and renewable resource on earth [5, 6]. Cellulose-clay nanocomposites are considered to be interesting functional materials with many potential environmental applications, biomedical fields and water treatment. There have been many reports on the synthesis of cellulose-clay nanocomposites. Mahamudur et al. [7] synthesized the cellulose-carbonated hydroxyapatite (CHA) nanocomposites by using cellulose solution, CaCl₂ and NaH₂PO₄. Yoshida et al. [8] synthesized the cellulose-CHA composites in situ through mechanochemical reaction

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using a conventional ball-mill.

Quanling Yang et al. [9] reported the preparation of cellulose-montmorillonite nanocomposite from cellulose/LiOH/urea solution.

Recently, another type of inorganic nanoparticle, layered double hydroxides (LDHs), called anionic clays, has attracted much attention. LDHs have been used as catalysts, ion exchangers and optical hosts in the preparation of polymer nanocomposites [10, 11]. Yadollahi et al. [12] synthesized carboxymethyl cellulose/LDH exfoliated nanocomposite films by casting carboxymethyl and LDH aqueous solution. Guolin et al. [3] prepared flame retardant form stable phase change materials composed by EPDM, paraffin and nano magnesium hydroxide.

Microwave synthesis method is used as a promising technology for the synthesis of many nanocomposites [13]. It is a rapid and green methodology. Another interesting synthesis method is the activation by ultrasonic radiation. Indeed, the application of ultrasonic to nanomaterials has multiple effects. The most obvious is the dispersing of materials in liquids in order to break particle agglomerates. Stoica-Guzun et al. [14] investigated the effect of ultrasonic irradiation on the calcium carbonate deposition on bacterial cellulose membranes using CaCl_2 and Na_2CO_3 as starting reactants.

In this work, the cellulose-based nanocomposites powder have been elaborated from microcrystalline cellulose (MCC) which has been reinforced with the synthetic clay Hydrotalcite MgAlCO_3 (family of layered double hydroxides HDL) as a nanofiller, using activation method by microwave or ultrasound in selected conditions. Activation method by microwave radiation was made using two protocols: the first one consists in the dispersion of fillers (Hydrotalcite HT) in NaOH/urea/MCC solution. The second protocol is based on the swelling of the MCC and HT separately with distilled water. These two solutions are then mixed together.

The ultrasonic activation method was made according to a single protocol which consists in the dispersion of cellulose in HT-solution (HT dissolved in 7%wt NaOH/12%wt urea aqueous solution) which had previously been homogenized by ultrasonic radiation.

A fourth process was also tested; it consisted in the preparation of the nanocomposite in situ by instantaneous coprecipitation of the hydrotalcite in the cellulose.

The aim of this study is to compare different protocols for obtaining a Hydrotalcite-cellulose nanomaterial and their structural properties.

II. MATERIAL AND METHODS

Microcrystalline cellulose (MCC) was obtained from Sigma-Aldrich. Salts of metals ($\text{MgCl}_2, 6\text{H}_2\text{O}$) and ($\text{AlCl}_3, 6\text{H}_2\text{O}$) with a content of 99%, pearl sodium hydroxide in the form of a content of 98% and sodium carbonate (Na_2CO_3) in a content 99,9% were provided by the LOBACHemie laboratory. The urea of 99% was provided by CHEMICAL.

II.1 Synthesis

II.1.1 Preparation of MgAlCO_3 Hydrotalcite HT

The MgAlCO_3 hydrotalcite was synthesized by coprecipitation at a controlled pH as described elsewhere [15]. Typically, 60.99g of ($\text{MgCl}_2, 6\text{H}_2\text{O}$) and 24.14g of ($\text{AlCl}_3, 6\text{H}_2\text{O}$) were dissociated in 300ml of distilled water and the solution was added dropwise to a solution of 32g of NaOH and 2.12g of Na_2CO_3 in 300ml of water, under vigorous stirring. Then after, the resulting suspension was refluxed at 70°C for 17 hours under vigorous stirring. The precipitated solid was collected, washed thoroughly with hot distilled water and dried at 70°C for 15 hours.

II.1.2 Preparation of MCC-HT nanocomposites

The synthesis of nanomaterial MCC-HT (MCC-MgAlCO_3) was performed using four protocols.

Process I: This protocol consisted in the dispersion of clay fillers HT- MgAlCO_3 in NaOH/urea/MCC solution. Microcrystalline cellulose (MCC) solution was prepared by the method described by Jia et al. [16]. In typical synthesis, both 28g of NaOH and 48g of urea were mixed in 320ml of distilled water under vigorous stirring, then, 8.14g of MCC were added. The mixture was then stirred for 12 hours and cooled to 5°C in a refrigerator. The obtained cellulose solution, which can be stored in the refrigerator for a maximum of one month, is used for the synthesis of nanocomposites MCC-HT. In this process, a 5% of hydrotalcite HT- MgAlCO_3 was dispersed in 95% cellulose solution

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(w/w). The reaction mixture was left under agitation for one night. The obtained solution was subjected to microwave radiation at 350 watt during 3 minutes, according to the optimal conditions previously found [17, 18] and then centrifuged at 3000 rpm for 12min. The synthesised was washed with a mixture of distilled water/ ethanol (50V/50V) and dried in an oven at 50°C for 7 hours.

Process II: In this process, three solutions were prepared: the first one is the cellulose solution CMC/NaOH/urea/H₂O (1.62g/3.5g/6g/40ml), which is stirred for 24 hours and then cooled to 5°C at which its is maintained for 12 hours. The second solution is the mixture of magnesium and aluminium salts prepared from 6.1g of MgCl₂·6H₂O and 2.4g of AlCl₃·6H₂O dissolved in 30ml of distilled water. The third solution contains 0.212g of Na₂CO₃ dissolved in 30ml of distilled water. Solution (1) is introduced in a three-necked flask of 1liter in which 320ml of distilled water have been previously placed. The (2) and (3) solutions are placed in funnels and added dropwise to the solution (1) under vigorous stirring at 50°C while the pH is maintained constant between 9 and 10. The resulting mixture is refluxed for 17 hours and cooled to ambient temperature; the precipitate is filtered and washed three times with distilled water at 80°C. The product obtained is dried in an oven at 65°C.

Process III: This protocol consisted in a separate swelling, of 0.1g hydrotalcite (HT3-MgAlCO₃) and 1.9g cellulose MCC in distilled water. The HT3-MgAlCO₃ and MCC solutions were stirred for 2 hours. The swelled samples are mixed and stirred at 40°C for 18 hours. The solution was treated with microwave energy for 3 minutes at 350W; the composite MCC-HT3-MgAlCO₃ synthesized has a creamy texture. The product is separated from the solution by centrifugation (12 min, 3500 rpm), then washed with distilled water and ethanol and dried at 60°C.

Process IV: NaOH/urea/H₂O (3.5g/6g/40mg:1/1.7/11.3) solution was prepared. A known amount of HT3-MgAlCO₃ was dispersed in the solution and stirred for 2 hours at room temperature. The suspension of hydrotalcite was sonicated for 8 min and then the solution was cooled to 7°C. The setting of the ultrasound device was as follows: Energy: 29254J, Power 65W, time 8min36, 50 continuous seconds, 10 seconds off. After cooling, a known amount of MCC is added to the solution so as to obtain a composite of 95% MCC and 5% HT3 and then the mixture is stirred overnight. The mixture is centrifuged at 3500 rpm for 12 min, washed with water/ethanol and dried at 60°C. The obtained nanocomposites cellulose-Hydrotalcite MCC-HT3.5% was denoted nano-Py, with P= protocol and y= 1, 2, 3 or 4.

III. CHARACTERIZATION

X-Ray powder diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR) were carried out to check the structural characteristics of HT3-MgAlCO₃, MCC and synthesized nanocomposites.

Powder XRD of the material was obtained by using Philips PW 1130/90 X-Ray diffractometer, available in our laboratory, with CuK α radiation (40KV and 20mA) at a scan rate of 1°/min in 2 θ ° range of 5-70.

The texture and the chemical composition of the samples are identified both by transmission electron microscopy (TEM) using the JEOL microscope 2010 and EDX (energy dispersion spectroscopy), it is available at National Center for Scientific and Technical Research (CNRST) in Rabat, Morocco. The powders were first suspended in ethanol and subjected for 3 min ultrasonic vibrations to break any agglomerates. The slurry is then deposited on a copper grid coated with a carbon membrane. Chemical analysis of the powders can be performed by energy dispersion spectroscopy EDX.

Fourier Transform Infrared (FTIR) spectroscopy was carried out on a JASCO4100 FTIR spectrophotometer, which was equipped with a detector TGS and a source of ceramics, separated by optical system using a Michelson interferometer, available to the common center of analyzes at the Faculty of Sciences Meknes, Morocco. Dried samples were ground with KBr to form pellets and the spectra were recorded in the range of 4000-400cm⁻¹ at 4cm⁻¹ resolution.

IV. RESULTS AND DISCUSSION

IV.1 X-Ray Diffraction (XRD) analysis

The diffraction patterns for MCC, HT3 (MgAlCO₃) and MCC-HT3 nanocomposites containing 5% of HT3 are shows

in fig.1.

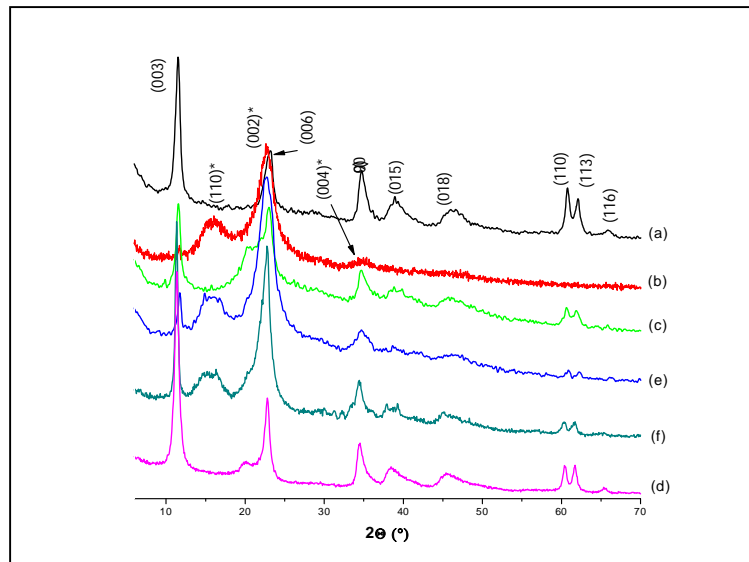


Fig. 1. XRD patterns of (a) HT3, (b) MCC, (c) nano-P1, (d) nano-P2, (e) nano-P3 and (f) nano-P4.

* Diffraction planes of MCC.

The diffraction patterns for HT3 ($MgAlCO_3$) (fig.1.a) shows the presence of all diffraction peaks (00l) which were characteristics of a lamellar structure comparable to those previously reported in the literature [15]. It indicates that the synthesised HT3 presents pure and well-crystallized hydrotalcite phase with a basal spacing of $d_{003}=7.71\text{\AA}$.

XRD pattern of MCC (fig.1.b) presents three diffraction peaks at $2\theta=16^\circ$, 22° and 34° assigned to (110), (002) and (004) diffraction planes, respectively [19]. The peak at $2\theta=16^\circ$ corresponds to amorphous cellulose while the peak at $2\theta=22^\circ$ and 34° correspond to the crystalline cellulose [20].

Fig.1.c shows XRD pattern of the sample (nano-P1) synthesized following the process I. The diffraction peaks are assigned to (003), (006), (009), (015), (018), (110), (113) and (116) planes corresponding to characteristic rays of Hydrotalcite samples [15].

Fig.1.d shows XRD pattern of the sample (nano-P2) synthesized by the coprecipitation method. The pattern indicates the presence of all diffractions peaks of the hydrotalcite and thus shows a well-crystallized hydrotalcite phase.

Both compounds nano-P1 and nano-P2 present the diffraction peak at $2\theta=20^\circ$ corresponding to the cellulose phase in a low polymerization state, in agreement with the result obtained by Haibo Zhao et al. [21]. It was observed that the decrystallization of cellulose (cotton) in trifluoroacetic acid at 65°C gives the peak at $2\theta=20^\circ$ when the degree of polymerization DP decreases. In our case, the dissolution of MCC in NaOH/urea medium is unfavorable to the dispersion of MCC with high DP in hydrotalcite phase.

In addition, for the composite nano-P1, the characteristic peaks of cellulose and hydrotalcite are broad indicating the formation of a poorly crystallized nanocomposite HT-MCC. However, the nanomaterial obtained by co-precipitation (nano-P2) had a better ordered and crystallized structure than nano-P1.

The XRD spectrum of synthesized MCC-HT3 ($MgAlCO_3$) nanocomposite by process III (nano-P3) is shown in fig.1.e. A low peak at $2\theta\approx 16^\circ$ and an intense peak at $2\theta\approx 22^\circ$ were observed and can be assigned to the typical peaks in MCC [22]. The broad peak around 22° is the superposition of two peaks, which can be assigned to the peak (002) at 22° in MCC and the peak (006) of HT3. The presence of all diffraction peaks (00l) characterizing Hydrotalcite structure with a very low intensity, shows the partially exfoliated nanostructure for MCC-HT3-5% nanocomposite obtained following the protocol III, it can be considered that when MCC and HT3 are swollen separately, the dispersion of the nanoparticles Hydrotalcite in cellulose lead to the partially exfoliated structure. This can be compared to the work of Yadollahi and al. [12] concerning the preparation of carboxymethyl cellulose/Layered Double Hydroxides

bionanocomposite through which they obtained an exfoliated/intercalated nanostructure for CMC-LDH nanocomposite. XRD spectra of MCC-HT3 nanomaterial elaborated according to the ultrasound method (nano-P4) is shown in fig.1.f. XRD peaks of the two phases are present. Indeed, the diffraction peak of HT3 (corresponding to d003) became more intense and very fine. The structure of the cellulose is retained with its two phases; amorphous (peak at $2\theta \approx 16^\circ$) and crystalline (peak at $2\theta \approx 22^\circ$). The peak at $2\theta \approx 22^\circ$ increased in intensity because it included the peak (006) of hydrotalcite and the peak (002) at 22° of cellulose. There has been a significant increase in the intensity of peaks of HT3 compared to other nanocomposites, indicating that ultrasonic-assisted method causes a reduction of aggregates and a good dispersion of nanoparticles of Hydrotalcite and consequently this process is favourable to the formation of cellulose-hydrotalcite nanocomposite in which the HT is dispersed into the MCC. There is also an observed peak of a low intensity at $2\theta = 40^\circ$, probably due to the formation of an additional phase.

The XRD results indicate that the cellulose-hydrotalcite (MCC-HT3) nanocomposites with 5% of renfort clay have been successfully elaborated by treatment for three minute via microwave-assisted method or by ultrasonic-assisted method, confirming the high reaction efficiency of this method.

IV.2 TEM characterization:

TEM images are used to have information on morphology, the phase distribution and exfoliation structure or mixed phase of HT/cellulose. Figure 2 presents the TEM images of cellulose MCC and Hydrotalcite HT3 used for the preparation of nanocomposites according the protocols I, III and IV.

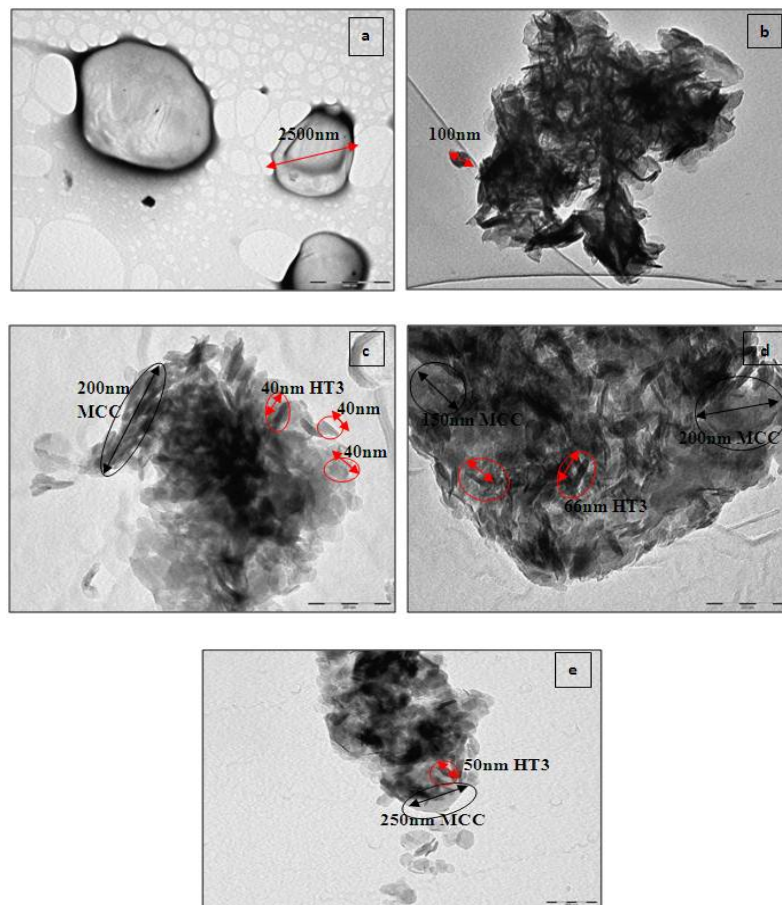


Fig. 2 TEM images of HT3 of (a) MCC, (b) HT3, (c) nano-P1, (d) nano-P3 and (e) nano-P4.

The large cellulose particles are clearly visible in Fig.2a. Fig.2b illustrates the TEM micrograph for MgAlCO₃hydrotalcite (HT3). The HT3 layers exist as individual layers or as agglomerated particles with particle size about 100 nm.

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IV.3 EDX characterization:

The atomic composition of the studied samples is presented in fig.3. It can be seen the heterogeneity of the atomic composition of the various nanomaterials developed. Indeed, magnesium, aluminium and carbon could be detected. The elemental composition deduced by EDX analysis shows the presence of the main elements (Mg, Al and C) which constitute the matrices for the different composites obtained (Table 1).

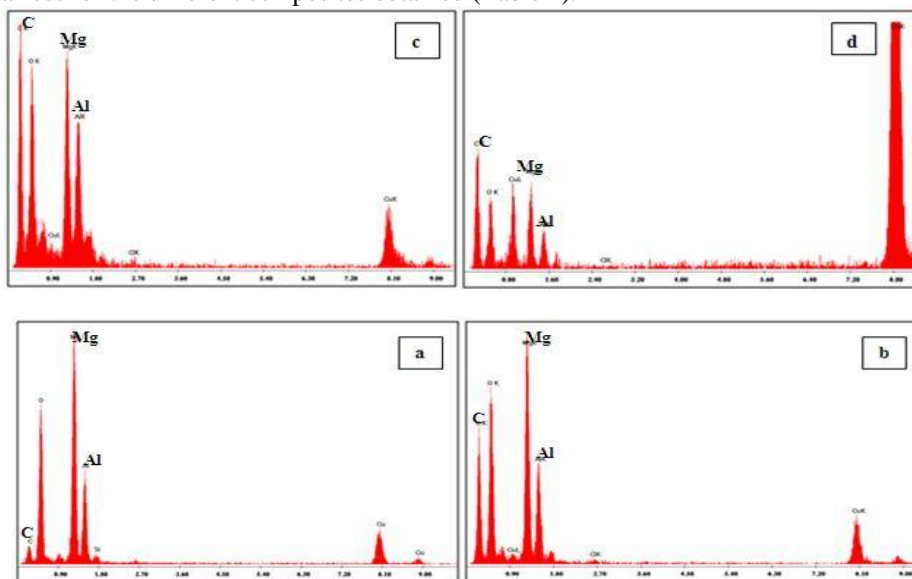


Fig. 3EDX analyses conducted on (a) HT3, (b) nano-P1, (c) nano-P3 and (d) nano-P4.

For nano-P1 and nano-P4 the Mg/Al ratio is equal to 2 and is near the Mg/Al for HT3, in accordance with the presence of the hydrotalcite phase observed by XRD. On the contrary, the nano-P3, which has a partially exfoliated structure, has the lowest Mg/Al ratio.

The Mg/C ratio confirms the presence of the carbon element with variable proportions depending on the type of the nanocomposite obtained (Table 1).

It should be noted that HT3 contains carbon which comes to carbonates of the hydrotalcite (Fig.3a).

Table 1. Ratio of the chemical elements

	HT3	Nano-P1	Nano-P3	Nano-P4
Mg/Al	2.4	2.2	1.5	2.2
Mg/C	-	1.6	0.9	0.7

IV.4 FTIR characterization

FTIR spectroscopy was used to detect the characteristic vibrations of new chemical bonds and show the type of interaction between phases in the nanomaterial. Figure 4 shows the IR spectra of HT3, MCC, nano-P1, nano-P2, nano-P3 and nano-P4, in the frequency range 4000-400 cm^{-1} .

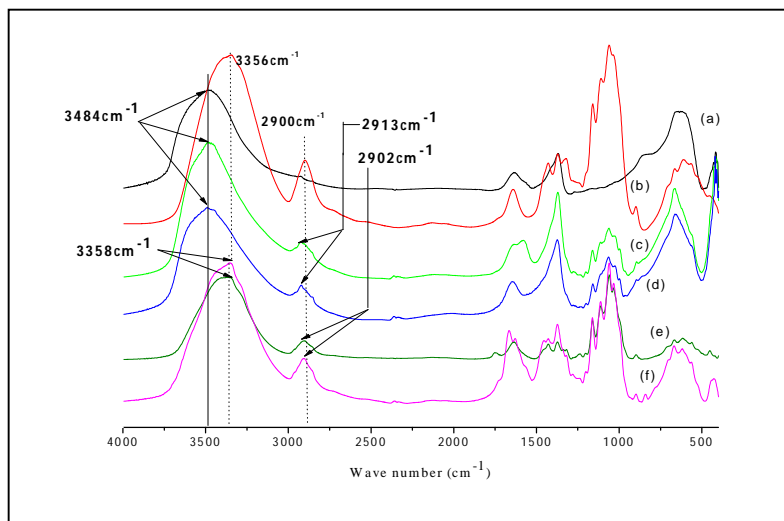


Fig. 4. FTIR spectrum of (a) HT3, (b) MCC, (c) nano-P1, (d) nano-P2, (e) nano-P3 and (f) nano-P4.

Fig.4.a shows the FTIR spectrum of HT3-MgAlCO₃. The characteristic bands and their attributions [15] are summarized in Table 2. FTIR spectrum of MCC (fig. 4b) exhibited the broad band centred at 3356 cm^{-1} , attributed to the stretching vibrations of -OH groups. The band at 2900 cm^{-1} corresponds to C-H vibrations in cellulose, who gives the deformed band at 1422 cm^{-1} . The absorption bands between 1000 and 1200 cm^{-1} were attributed to the C-O stretching on the polysaccharide skeleton [23].

Table 2: Main vibrations bands of HT3 and their attributions

Bands (cm^{-1})	Attributions
3481	$\nu_{as}(\text{OH})$
1644	$\delta(\text{H}_2\text{O})$
1360; 982	$\nu_{as}; \nu_s(\text{CO}_3)$
700-500	$\nu(\text{M-O-M})$

FTIR spectrum of all nanocomposites P1, P2, P3 and P4 shows the characteristic bands of both cellulose and the Hydrotalcite HT3. The main changes observed are the differences in the positions of O-H and C-H groups and the intensity of vibration band à 1360 cm^{-1} characteristic of carbonate species:

- The appearance of the O-H band for nano-P1 and nano-P2 at the same position as hydrotalcite at to near 3480 cm^{-1} , indicate the predominant hydrotalcite phase in the nanocomposite. While for nano-P3 and nano-P4, the position of this band is close to that of cellulose (3364 cm^{-1} and 3415 cm^{-1} respectively), which lets consider a predominance of cellulose phase. These findings are in agreements with the observations of XRD.
- The absorption band at 2900 cm^{-1} assigned to the vibration of C-H stretching in the cellulose is moved toward 2913 cm^{-1} for nano-P1 and nano-P2 (Fig.4c and d) and the intensity of this band decreases significantly (Table 3). It is indicating the presence of the cellulose sample in a low state of polymerization (in accordance with the result obtained by XRD). A similar result was obtained by Diana Ciolacu et al. [24] in the preparation of the amorphous cellulose from different types of celluloses (microcrystalline cellulose, dissolving pulp and cotton cellulose). These authors observed a

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shift of the vibration band C-H from 2899 cm^{-1} to 2924 cm^{-1} when the degree of polymerization DP passes from 183 to 178.

- For MCC-HT3 nanocomposite obtained by Process III, the carbonates species of the hydrotalcite (1360 cm^{-1}) have a low intensity. In addition, the ratio $I_{\text{vCH}}/I_{\text{vCO}_3}$ is the highest and the ratio $I_{\text{vCO}_3}/I_{\text{vOH}}$ is the lowest (Table 3). This shows that the obtained nanomaterial is constituted of a major phase of MCC and a small phase of HT3, thus confirming the hypothesis of a partially exfoliated structure observed by XRD.

- However, for MCC-HT3 nanomaterial elaborated by the ultrasonic method (nano-P4), it is observed a broad and intense band -CH centred at 3458 cm^{-1} which regroups probably both bands C-H of MCC and HT3 (Fig.4f). This is confirmed by the evolution of the intensity of -CH band, characteristic of the cellulose, compared to the intensity of the vibration band of carbonate group of the HT3. In this case, the intensity ratio $I_{\text{vCH}}/I_{\text{vCO}_3}$ is important and close to 1 (Table 3) and shows therefore a significant presence of two phases (cellulose and Hydrotalcite).

Table 3: Evolution of $I_{\text{vCH}}/I_{\text{vCO}_3}$ and $I_{\text{vCO}_3}/I_{\text{vOH}}$ for elaborated nanocomposites through the different processes.

	Process I	Process II	Process III	Process IV
$I_{\text{vCH}}/I_{\text{vCO}_3}$	0.19	0.25	1.86	1.09
$I_{\text{vCO}_3}/I_{\text{vOH}}$	0.65	0.66	0.09	0.17

V. CONCLUSION

In this study we were interested in preparing an organic-inorganic nanocomposite (microcrystalline cellulose MCC-Hydrotalcite MgAlCO_3) by adopting different methods and at a structural analysis of each obtained nanomaterial. To this end, four protocols (P1, P2, P3 and P4) were tested. The resulting materials were characterized by XRD, IR spectroscopy and transmission electron microscopy (TEM). The results obtained show that:

- The process of dissolution of the hydrotalcite MgAlCO_3 in the cellulose solution NaOH-urea (P1) and the process consisting in coprecipitating the salts of Mg and Al with NaOH in a solution of cellulose (P4), led to a nanocomposite having a mixed phase (Hydrotalcite-MCC) with the cellulose phase in a lower degree of polymerization DP. However, the nano-P1 has a lower crystallinity than nano-P2;

- The swelling of the hydrotalcite and the cellulose in an aqueous solution (P3) followed by activation by microwave, yielded a nanocomposite with a partially exfoliated structure. The XRD showed the sharp decrease of intensity of all peaks (001) characteristic of hydrotalcite phase;

- The prior treatment of the hydrotalcite MgAlCO_3 ultrasonically (P4) before being brought into contact with the cellulose, gives a nanomaterial composed of two phases (cellulose and hydrotalcite), with almost equal proportions of each phase;

- Consequently, the synthesis methodology has a high influence on the structure and probably on the properties of MCC-HT3 nanocomposites elaborated.

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