



EFFECT OF COMBINED MICROWAVE-ULTRASOUND IRRADIATION IN THE STRUCTURE AND MORPHOLOGY OF HYDROTALCITE LIKE COMPOUNDS Al/Mg-CH₃COO AND ITS EVALUATION IN THE SORPTION OF A REACTIVE DYE
EFEECTO DE LA IRRADIACIÓN COMBINADA DE MICROONDAS-ULTRASONIDO EN LA ESTRUCTURA Y MORFOLOGÍA DE COMPUESTOS TIPO HIDROTALCITA Al/Mg-CH₃COO Y SU EVALUACIÓN EN LA SORCIÓN DE UN COLORANTE REACTIVO

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Received: March 02, 2019; Accepted: June 29, 2019

Abstract

Textile effluents contain a great variety of dye residues, their presence in the environment is undesirable since they cause a severe contamination in the aquifers. Different technologies are commonly used in the removal of these kind of dyes, which are often recalcitrant due to their anionic character, such as the sorption with activated carbon, zeolites and recently anionic clays (hydrotalcite-like compounds Al/Mg(HT-Al/Mg)) with relatively good results. The HT-Al/Mg can be synthesized by various methods assisted by treatments in the crystallization stage such as microwave and/or ultrasound irradiation, which allow the control of textural and morphological properties, in addition to reducing the synthesis times. The effects on the texture and morphology properties of HT-Al/Mg with an organic interlamellar anion (CH₃COO⁻) synthesized by coprecipitation assisted with microwave irradiation, ultrasound and microwave-ultrasound in combined mode are studied. The synthesized materials were evaluated in the sorption of the reactive dye BEZAKTIV Red S-LF with reference to activated carbon. The solids were characterized before and after evaluation by known techniques described below. It was found that the HT-Al/Mg-CH₃COO irradiated by the combined mode had the highest capacity of removal of the dyes compared to the reference material and when the materials were irradiated separately by microwaves or ultrasound.

Keywords: hydrotalcite-like compounds, hydrotalcites morphology, hydrotalcites texture, microwave and/or ultrasound irradiation synthesis.

Resumen

Los efluentes textiles contienen una gran variedad de residuos de colorantes, su presencia en el medio ambiente es indeseable ya que ocasionan una severa contaminación de mantos acuíferos. Comúnmente se utilizan diferentes tecnologías para la remoción de colorantes, que suelen ser recalcitrantes debido a su carácter aniónico; como la sorción con carbón activado, zeolitas y recientemente, arcillas aniónicas como los compuestos tipo hidrotalcita Al/Mg(CTH-Al/Mg). Los CTH-Al/Mg pueden ser sintetizados por diversos métodos asistidos por tratamientos en la etapa de cristalización como la irradiación microondas y/o ultrasonido, que permiten el control de propiedades texturales y morfológicas, además de disminuir los tiempos de síntesis. Por tal motivo se estudian los efectos en la textura y morfología de CTH-Al/Mg con un anión interlamellar orgánico (CH₃COO⁻), sintetizados por coprecipitación asistida con irradiación microondas, ultrasonido y microondas-ultrasonido en modo combinado. Los materiales sintetizados se evaluaron en la sorción del colorante reactivo BEZAKTIV Rojo S-LF tomándose como referencia carbón activado. Los sólidos se caracterizaron antes y después de la evaluación por técnicas conocidas. Se encontró que el CTH-Al/Mg-CH₃COO irradiado por modo combinado tuvo la mayor capacidad de remoción del colorante en comparación del material de referencia y de los compuestos irradiados con microondas o ultrasonido.

Palabras clave: compuestos tipo hidrotalcita, morfología de hidrotalcitas, textura de hidrotalcitas, síntesis por irradiación microondas y/o ultrasonido.

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<https://doi.org/10.24275/rmiq/Mat567>

issn-e: 2395-8472

1 Introduction

Hydrotalcite-like compounds (HT) are lamellar solids belonging to the family of anionic clays and have been of great importance in recent years due to their potential application in catalysis, medicine and as sorbents of pollutants in treated water since they possess a high anionic selectivity, which allows its use for removal of specific anions such as those present in textile reactive dyes. However, its scarcity in nature has promoted the synthesis of these materials with new and better synthesis techniques such as the use of microwave irradiation and / or ultrasound in the crystallization stage (Abdelkader *et al.*, 2011; Paredes *et al.*, 2015).

HT are formed by double hydroxides (Fig. 1) whose laminae are similar to brucite [$\text{Mg}(\text{OH})_2$], and are represented by the general formula $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2] [\text{A}_{x/n}^{n-}]_n \cdot n\text{H}_2\text{O}$, M (II) is a divalent metal (Mg, Zn, Ni, Cu, Co, etc.); M (III) is a trivalent metal (Al, Cr, Ga, Fe, etc.); $\text{A}_{x/n}^{n-}$ is an organic compensation anion (acetates, carboxylates, phosphates, glycerates, etc.) or inorganic compensation anion (CO_3^{2-} , SO_4^{2-} , Cl^- , NO_3^- , etc.) with charge n , and x is the molar metal ratio (M(III)/(M(III)+ M(II))) with values from 0.2 to 0.33, within this interval the structure of the HT remains stable (Shu-Ping *et al.*, 2006; Ocadiz 2015; Zarazua 2018).

HT can be synthesized by various methods such as: sol-gel (Ramos *et al.*, 2015), anion exchange (Constantino *et al.*, 2005), reconstruction of the structure (Ardanuy *et al.*, 2011) and coprecipitation (Paredes *et al.*, 2015), the latter being the most used. These methods can be assisted in the crystallization stage by various treatments such as: thermal conduction (Rivera *et al.*, 2006), microwave or ultrasound irradiation (Morales *et al.*, 2018, Zarazua *et al.*, 2018; Paredes *et al.*, 2015). The coprecipitation method consists of the simultaneous addition of an alkaline solution and a solution containing the mixture of metal precursors under controlled conditions of pH, pressure and temperature in an inert atmosphere (N_2) (Bosch *et al.*, 2006; 2015). Where the thermal treatment by conduction (which works at temperatures between 60-150 °C, for times ranging between 24 and 72 h) allows to obtain a material with morphological characteristics (growth of crystals) and textural (crystallinity, porometry, surface area) limited; while the use of microwave or ultrasound irradiation allows the control of these properties, which depend on the precursors, the power and frequency of irradiation; in addition to reducing the synthesis time from hours to minutes compared to the thermal treatment by conduction or convention (Cavani 1991, Bouraada *et al.*, 2008, Paz 2014, Paredes *et al.*, 2015; Zarazua 2018).

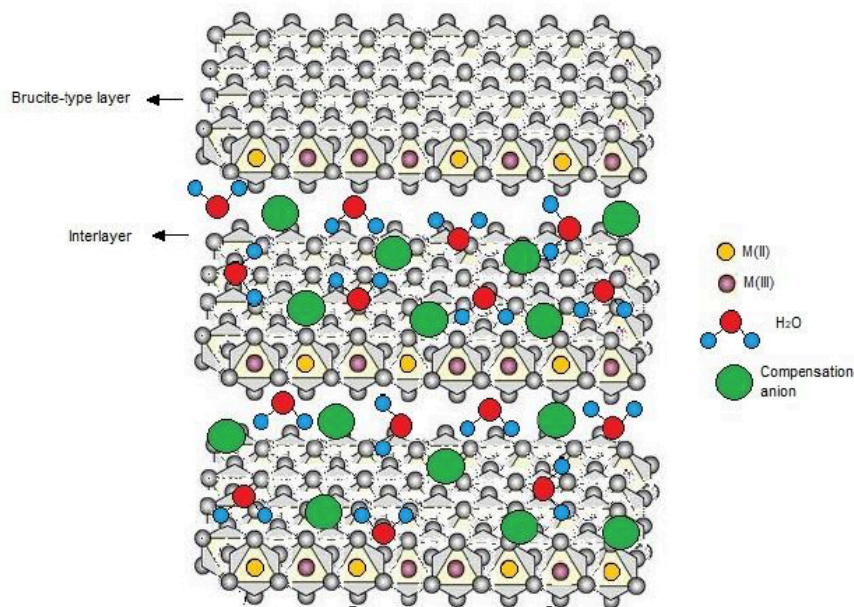


Fig. 1. Structure of Hydrotalcite-like compounds (HT).

The microwave irradiation is formed by electromagnetic waves that transfer energy directly to the reactants, when the dipoles of these try to align themselves to the electric and/or magnetic field, overheating occurs due to the molecular movement of the ions and the rotation of the dipoles, promoting the crystallization and growth of crystals in preferential directions (001) for the case of the HT (Bosch *et al.*, 2006, Zuñiga 2015, Zarazua 2018). For its part, ultrasound irradiation generates high pressures and temperatures at defined points within the solution due to the creation, expansion and implosion of small bubbles (cavitation) that are formed by the expansion and compression of sound waves through the medium, this causes the rupture of the links favoring the formation of crystals in all directions with specific characteristics (Shen 2009, Paz 2014, Paredes *et al.*, 2015, Zarazua 2018).

In this work we studied the textural and morphological effect in the crystallization stage by the use of microwave, ultrasound and microwave-ultrasound (combined mode) irradiation method in the synthesis of HT-Al/Mg with interlamina acetate anion (CH_3COO^-) by coprecipitation at constant pH. The obtained were solids characterized and evaluated in the sorption of reactive dyes, which are anionic, highly soluble in water and are resistant to aerobic biodegradation in the conventional removal processes, they present serious problems of toxicity causing severe contamination in rivers and groundwater, and in large quantities cause difficulty in breathing, nausea, vomiting, diarrhea and even develop some types of cancer (Colindres 2010). The reactive dye BEZAKTIV Red S-LF (Fig. 2) will be taken as a model molecule, since it is one of the most used in the textile industry.

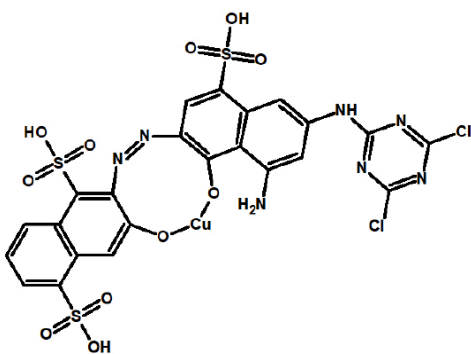


Fig. 2. Structure of reactive dye BEZAKTIV Red S-LF.

When we have an organic anion in the interlamina in the HT (Fig. 1), it is expected that a greater interlamina spacing will be generated that promotes the anion exchange, additionally and according to the proposed synthesis technologies we expect to improve morphological and textural properties that facilitate the diffusion process in the available spaces during the sorption when compared with hydrotalcites with inorganic compensation anions prepared by thermal conduction and with adsorbent materials such as activated carbon.

2 Experimental

2.1 Materials and methods

HT-Al/Mg- CH_3COO with a molar metal ratio of 0.25 were synthesized according to the following procedure. An aqueous solution of sodium hydroxide [NaOH] (J.T. Baker, 97%) 1M and an aqueous solution of magnesium acetate [$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] (98%, Sigma Aldrich) and aluminum acetate [$\text{AlOH}(\text{CH}_3\text{COO})_2$] (100%, Sigma Aldrich) in a 4:1 ratio were subjected to coprecipitation at room temperature in an inert atmosphere of N_2 , controlling the pH to 11 ± 0.2 . The gel obtained was separate in three equal volumes and irradiated in a SBL-CW-2000A microwave/ultrasound reactor by microwave (800 W, 2.4 GHz) and ultrasound (50 W, 40 KHz) in simultaneous mode (microwave-ultrasound) for 5 minutes. It should be mentioned that this reactor is capable of simultaneously irradiating microwaves and ultrasound; the basic function of microwaves is to provide thermal energy to the reactor and the ultrasound irradiation as a means of agitation. The samples were washed with distilled water and dried at 70°C for 72 hours; they were identified according to Table 1 (Paredes *et al.*, 2015, Zarazua 2018).

Table 1. Identification name of synthesized samples.

Sample	Name
HT-Al/Mg- CH_3COO microwave	Ac-m
HT-Al/Mg- CH_3COO ultrasound	Ac-u
HT-Al/Mg- CH_3COO combined	Ac-mu

2.2 Characterization

The synthesized compounds were characterized by X-ray diffraction (XRD), nitrogen physisorption (BET), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD spectra were obtained on a PANalytical model X Pert PRO diffractometer for thin films or crystalline coatings ($\lambda = 1541 \text{ \AA}$). By nitrogen physisorption at 77K, the specific area was determined by the BET model, volume and pore size distribution by the BJH model, the isotherms were obtained in a NOVA 4200e equipment of the Quantumchrome Instruments brand with a pretreatment at 100 °C by 20 hours. The infrared spectra were obtained on a Nicolet Magna-IR 550 spectrometer in a range of 4000-650 cm^{-1} . The SEM micrograms were obtained in a JEOL scanning electron microscope model JSM7800 F at 1.5 kV. The TEM micrograms were obtained in a transmission electron microscope JEOL brand JEM-ARM200CF model at 0.1 kV.

2.3 Reactive dye sorption

The evaluation in the sorption of the synthesized materials, was carried out for the reactive dye BEZAKTIV Red S-LF (CHT BEZEMA), taking the activated carbon as a reference material. The quantification of the amount of sorbed dye was carried out by UV-Vis spectroscopy, in a double-beam spectrometer Dynamica model Halo DB-30 and in 10 mm quartz cells. Previously a calibration curve of 10-100 mg/L was made, starting from a solution at 100 mg/L at a $\lambda_{max} = 520 \text{ nm}$.

A 100 mL solution of 50 mg/L (BEZAKTIV Red S-LF/distilled water) was prepared by adding 0.1 g of HT-Al/Mg- CH_3COO synthesized by microwave, ultrasound, microwave-ultrasound and activated carbon (ratio 1 g/L) respectively. The average equilibrium time was 120 min, aliquots of 3 mL were taken by triplicate every 20 minutes in each case, the absorbance was measured at a $\lambda_{max} = 520 \text{ nm}$. The above procedure was repeated at 10, 25, 50, 75 and 100 mg/L (BEZAKTIV Red S-LF/distilled water). The quantity of sorbed pollutant in the materials evaluated at any time (q_t) ($\text{mg}_{\text{sorbate}}/\text{g}_{\text{sorbent}}$) was found according to Eq. (1) (Soetaredjo *et al.*, 2018).

$$q_t = \frac{V(C_o - C_t)}{m} \quad (1)$$

where V is the volume of the solution (L), C_o and C_t are the initial concentrations and time t (mg/L)

respectively and m is the mass of sorbent (g).

2.3.1 Sorption equilibrium studies (maximum sorption capacity)

In the study of sorption equilibrium, Langmuir and Freundlich isotherms (Soetaredjo *et al.*, 2018; Doaud *et al.*, 2017) were used to determine the maximum sorption capacity of materials; the results were fitted to the following non-linear equations, Langmuir (Eq. (2)) and Freundlich (Eq. (3)).

$$q_e = q_{max} \frac{k_L C_e}{1 + k_L C_e} \quad (2)$$

$$q_e = k_f C_e^{\frac{1}{n}} \quad (3)$$

In Eq. 2, q_e ($\text{mg}_{\text{sorbate}}/\text{g}_{\text{sorbent}}$) represents the sorption capacity at equilibrium, q_{max} ($\text{mg}_{\text{sorbate}}/\text{g}_{\text{sorbent}}$) is the maximum sorption capacity of the material, k_L is the sorption affinity constant, i.e., how strong the sorbate molecules are retained in the sorbent (L/mg); and C_e is the concentration of the solution in the equilibrium time (mg/L) (Soetaredjo *et al.*, 2018).

In Eq. 3, q_e is the same above, k_f is the sorption constant and is related to the positive value of the energy needed to complete the sorption until equilibrium is reached ($\text{mg}_{\text{sorbato}}/\text{g}_{\text{sorbente}}(\text{L}/\text{mg})^{1/n}$) and n is the Freundlich constant, which represents the relation of the degree of linearity between the sorption and the concentration of the solution; if $n < 1$, a chemisorption is performed and if $n > 1$ will be a physisorption (Doaud *et al.*, 2017; Rouquerol *et al.*, 2014).

The k_L value deduced from the Langmuir model (Eq. (2)), the degree of affinity (R_L) between the sorbate and the sorbent can be obtained using Eq. (4), if $0 < R_L < 1$ the pollutant sorption process is feasible in the sorbent materials, if $R_L > 1$ the sorbent material is not suitable to reach the sorption, if $R_L = 1$ the sorption is linear and if $R_L = 0$ the sorption is irreversible (Garcia *et al.*, 2014).

$$R_L = \frac{1}{1 + k_L C_o} \quad (4)$$

3 Results and discussion

The results and the discussion are presented in the following order. Firstly, the analysis related to the

sorption of the dye in the synthesized materials and the activated carbon as a reference are presented; secondly, the results concerning the textural and morphological characterization of the HT before and after the dye sorption are discussed.

3.1 Reactive dye sorption in HT

In Fig. 3 are shown the sorption profiles of BEZAKTIV Red S-LF as a function of time (t) and as a function of the initial content of reactive dye. The sorption is expressed as sorbent amount (q_t) of the reactive dye at different concentrations in the HT-CH₃COO synthesized by different treatments in the crystallization stage: a) combined mode, b) microwave, c) ultrasound and d) activated carbon as a reference material.

In all cases, the sorption equilibrium was obtained in 120 min at concentrations higher than 50 mg/L, for lower dye concentrations the equilibrium was reached at ~20 min, it is worth mentioning that a longer time was employed and the same results of 120 min were obtained. On the other hand, when it is compared the crystallization method, it was found a strong dependency with the quantity of contaminant sorbed, such that the highest sorption capacity at

100 mg/L was reached by a) Ac-mu (microwave-ultrasound) with 78 mg_{sorbent}/g_{sorbate}, followed by b) Ac-m (microwave) with 63.5 mg_{sorbent}/g_{sorbate}, c) Ac-u (ultrasound) with 49.7 mg_{sorbent}/g_{sorbate} and d) activated carbon with 26.4 mg_{sorbent}/g_{sorbate}. In the case of activated carbon, the sorption does not increase with the increase in the initial concentration of the dye, which indicates that the material is saturated at approximately 26 mg_{sorbent}/g_{sorbate}.

Sorption equilibrium studies (maximum sorption capacity)

The parameters of the Freundlich and Langmuir isotherms are summarized in Table 2. In all cases, R² is above 0.94, which indicates that there is a good correlation between the experimental data and equations.

With respect to the Langmuir model, the value of the maximum absorption capacity in the Ac-mu sample is greater than the other materials, which indicates that the combined irradiation (microwave-ultrasound) method induce an adequate morphology and texture that allowed a greater capacity of sorption in the dye, in comparison with the samples Ac-m (microwaves) and Ac-u (ultrasound) and the activated carbon had the smaller capacity of sorption.

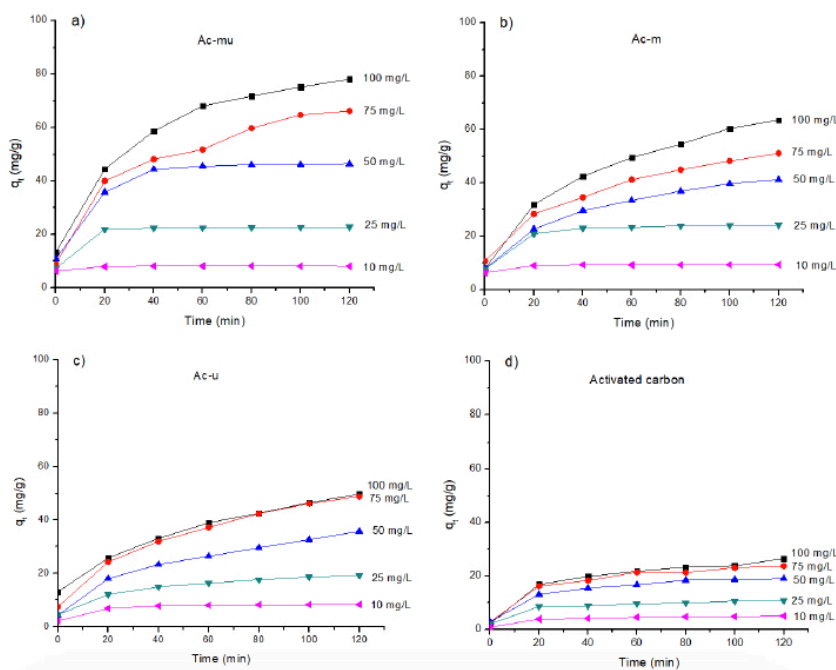


Fig. 3. Sorption profiles (time vs q_t) of the reactive dye BEZAKTIV Red S-LF at different concentrations in the HT-Al/Mg-CH₃COO: a) combined mode (Ac-mu), b) microwave (Ac-m), c) ultrasound (Ac-u) and d) activated carbon.

The k_L parameter related to the affinity indicates that the contaminant retention capacity in the studied sorbents is affected by the morphological and textural characteristics obtained by the synthesis method. The lowest affinity is the hydrotalcite irradiated in a combined mode, followed by the compounds irradiated by microwaves and ultrasound, the activated carbon is the one with the highest k_L value. The parameter R_L is greater than zero and less than one, that is to say, the sorption is favorable in all the cases, while the value of the n parameter which is related to the heterogeneity of the system is greater than 1, which indicates that the interaction between the sorbent and sorbate was physisorption (Daoud *et al.*, 2017; García *et al.*, 2014).

In the case of the Freundlich model, the lower values of k_F parameters correspond to the Ac-mu sample, which indicates that less energy is needed to carry out the sorption and its magnitude is close to the one of the activated carbon, the value of k_F increases in the Ac-m and Ac-u samples as a consequence the needed energy to carry out the sorption is higher.

The parameters obtained from the Langmuir and Freundlich isotherms are affected by the irradiation method used in the crystallization stage, the morphology and texture of the combined irradiated compound favors the sorption. In order to confirm this statement, the morphological and textural characterization of the materials evaluated is presented below.

3.2 Characterization

3.2.1 Scanning electron microscopy (SEM)

Fig. 4 shows micrographs of SEM at 20000X of the synthesized hydrotalcites: a) Ac-m, b) Ac-u and c) Ac-mu.

A porous laminar morphology with planar defects is observed in all the synthesized compounds, and it can be seen that the surface of the sample a) Ac-m is uniform, while in the sample b) Ac-u shows more irregularity due to the implosions caused by the cavitation effect during the synthesis; on the other hand, the sample c) Ac-mu presents a surface similar to the Ac-m sample, which probably indicates that the morphology obtained by microwaves predominates when combining the irradiation with ultrasound and works as a diffusion medium so that the sorption.

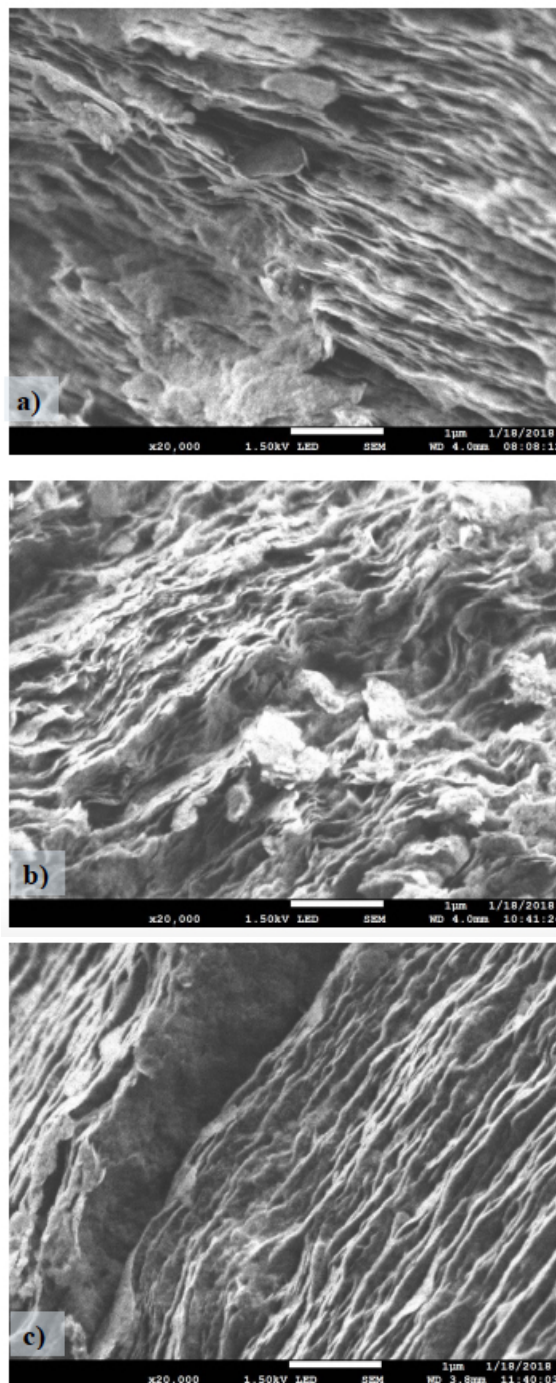


Fig. 4. SEM micrographs of synthesized HT-Al/Mg-CH₃COO: a) Ac-m, b) Ac-u and c) Ac-mu.

3.2.2 Nitrogen physisorption

Fig. 5 shows (a) the adsorption-desorption isotherms of N₂ and (b) the pore diameter distribution of the synthesized hydrotalcites are presented.

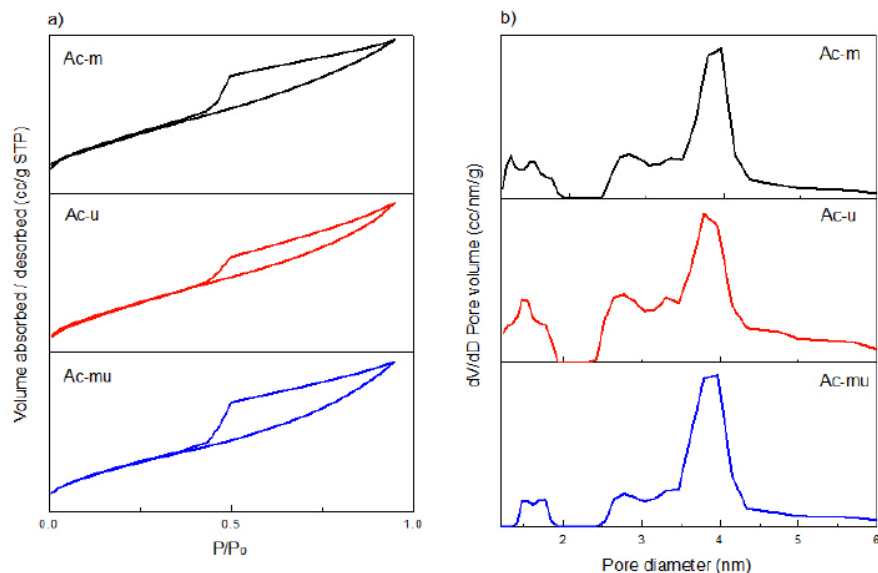


Fig. 5. a) Adsorption-desorption isotherms of N_2 and b) distribution of pore diameter of HT-Al/Mg- CH_3COO synthesized.

It is observed in Fig. 5 a) that the three compounds present an isotherm type IV, which is characteristic of mesoporous solids with hexagonal structure, and a hysteresis type H2 that is characteristic of materials with pores arranged as channels or sheets (Otero 2015). In Fig. 5 b) the synthesized compounds have a similar pore diameter distribution, although the compounds irradiated by microwaves (Ac-m) and ultrasound (Ac-u) are less uniform than the compound (Ac-mu), which has a more uniform pore diameter distribution of between 3 and 4.5 nm. Table 3 shows the values of surface area, size and pore volume of synthesized HT and activated carbon* (Ruthven 1984).

The compound irradiated with ultrasound (Ac-u) has a greater surface area and a larger pore volume followed by the Ac-m and Ac-mu samples; when irradiated with ultrasound, the effect of cavitation makes the surface very uneven causing defects of step and notch, obtaining a greater surface area and a larger pore volume (Zarazua 2018). By combining microwave-ultrasound (Ac-mu) irradiation, a decrease in surface area and pore volume is observed, this is probably attributed to the fact that the predominant morphology in the combined mode is that obtained by microwave effect. The largest pore diameter is found in the combination-irradiated compound (Ac-mu), while the diameter values in the Ac-m and Ac-u samples are very similar, indicating that combined microwave-ultrasound irradiation used in the crystallization stage

increases the pore diameter (Bosch *et al.*, 2006; Paredes *et al.*, 2015; Zarazua 2018). Figure 6 shows in a graphic way the relation of the percentage of removal of the BEZAKTIV Red S-LF dye and the surface area of the obtained compounds compared with the reference material (activated carbon). It can be seen that the sorption is independent of the surface area since the sample with more area is the one that has sorbed less dye, it is dependent on the type of irradiation used in the crystallization stage during the synthesis process. When irradiated in combined mode (Ac-mu), the largest pore diameters (Table 3) and uniform size are obtained (Fig. 5b), which allows the exchange sites to be more exposed (Al^{+3} in the brucite-type layer), which efficiently promote the exchange of the acetate ions by the anionic dye species, favoring the sorption (Newman *et al.*, 1998).

3.2.3 Fourier-transform infrared spectroscopy (FTIR)

The infrared spectra of the HT synthesized with interlaminal acetate component (Ac-m, Ac-u and Ac-mu), before and after the evaluation in the dye sorption are presented in Fig. 7 a) and the comparison of the spectrum of Ac-mu sample before and after the sorption with the IR spectrum of the dye is shown in the region of interest between 900 and 1800 cm^{-1} in Fig. 7 b).

In Fig. 7 a) a change in the intensity of the signals of the samples synthesized after the evaluation in the dye sorption is observed, it is seen in all cases that the signal at 3389 cm^{-1} related to the association of water with the brucite-type layer increases, while the signal at 1558 cm^{-1} related to interlamellar water decreases which could indicate that there was an anion exchange (Bouraada *et al.* 2008, Pokhriyal *et al.*, 2017).

In Fig. 7 b) the infrared spectrum is observed before and after the sorption of the Ac-mu sample, which showed greater removal capacity (Table 2), and it is compared with the spectrum of the dye. The decrease of the signal corresponding to interlamellar water (1558 cm^{-1}) is clearly shown and signals in wavelength 1481 , 1291 and 1118 cm^{-1} with low intensity corresponding reactive dye, are presented after the sorption. It is therefore deduced that the dye is found in the interlayer of the HT (Ahmed *et al.*, 1995, Mao *et al.*, 2005; Saaed *et al.*, 2014). Additionally, it is very clear that the $\nu_{\text{asym}}(-\text{COO}-)$ and $\nu_{\text{sym}}(-\text{COO}-)$ signals observed in ~ 1550 and $\sim 1400\text{ cm}^{-1}$ assigned to carboxyl vibrations disappear after the ionic interchange.

3.2.4 X-ray Diffraction (XRD)

In Fig. 8 the diffractograms of the Ac-m, Ac-u and Ac-mu synthesized samples before and after the dye sorption are shown. In all cases, the characteristic reflections of the HT are observed according to card 22-0700 of the Joint Committee on Powder Diffraction and Standards (JCPDS) corresponding to a two-dimensional hexagonal structure (Panda *et al.*, 2008; Samuei *et al.*, 2016).

The continuous line representing the XRD patterns of the hydrotalcite-like compounds are shown before been evaluated and it is observed that the intensity of the reflections are affected by the irradiation with which the synthesis was assisted in the crystallization stage. According to the height and width of the signals, the crystallinity of the sample irradiated by

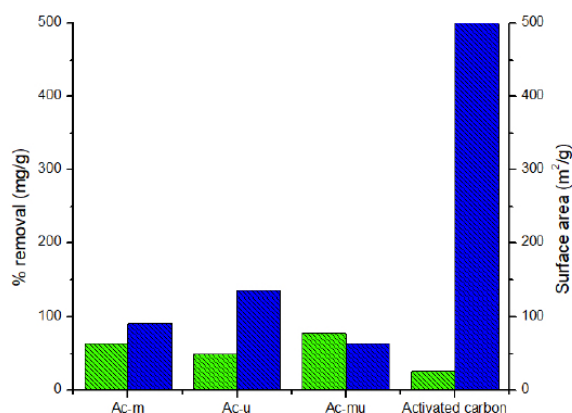
microwave (Ac-m) is greater than that irradiated by ultrasound (Ac-u); the sample irradiated in combine mode (Ac-mu) has a similar crystallinity to the sample irradiated by microwaves, this is because the microwaves predominate in the crystallinity of the HT when combined with ultrasonic irradiation. When evaluating the compounds obtained in the dye sorption (dashed line) no additional signals are observed but a change in the intensity and position of the reflections of the planes (003) and (006), related to the crystal size and the interplanar distance. In the Ac-u sample, the change in position and significant intensity (Figure 8) was not observed since this sample presented lower sorption capacity (Table 2), the sample irradiated with microwaves (Ac-m) showed a slight displacement, but the shift of 003 plane of the sample Ac-mu is highly remarkable, which was the one with the highest sorption capacity. Particularly, in the Ac-mu sample, the signals corresponding to the planes (003) and (006) increased the intensity more significantly and had a shift of 0.5° to the left in the angle 2θ , which is an indication of the increase in the interplanar distance that correspond with the interlamellar layer, so that the anionic species of the dye remained in the interlayer and in the available spaces. The values of the interplanar distance (d) and the crystal size (t) of the synthesized compounds before and after the evaluation in the dye sorption are summarized in Table 4. The sample synthesized by microwave irradiation (Ac-m), the alignment of the molecules with the electromagnetic waves inhibits the growth of the crystal but favors the spacing between the layers; on the other hand, when the compound is synthesized by ultrasound irradiation (Ac-u), cavitation phenomenon increases the collisions, which generates a smaller interplanar distance and a rugged surface (Fig. 4 b) with a similar crystal size. When comparing Ac-m and Ac-u samples with Ac-mu sample, the combine method causes a cooperative effect in some properties, in this case the interplanar distance is similar but there is a small increase in the crystal size.

Table 2. Parameters obtained from the Langmuir and Freundlich isotherms.

Sample	Langmuir				Freundlich		
	q_{max} (mg/g)	k_L (L/mg)	R_L	R^2	k_F (mg/g(L/mg) $^{1/n}$)	n	R^2
Ac-m	141.78	0.0079	0.588-0.926	0.99	2.277	1.38	0.98
Ac-u	104.42	0.0101	0.497-0.908	0.97	2.273	1.455	0.94
Ac-mu	322.68	0.0039	0.719-0.962	0.99	1.474	1.149	0.98
Activated carbon	49.89	0.0117	0.460-0.895	0.99	1.369	1.532	0.97

Table 3. Surface area, size and pore volume of HT-Al/Mg-CH₃COO synthesized.

Sample	Surface area (m ² /g)	Pore volume (cc/g)	Maximum pore diameter (nm)
Ac-m	91.35	0.1	4.61
Ac-u	135.2	0.15	4.55
Ac-mu	64.27	0.09	5.39
Activated carbon*	1000	0.5	2

Fig. 6. Relationship between the percentage of removal vs surface area of synthesized HT-Al/Mg-CH₃COO and activated carbon.

In addition, based on the results of the textural analysis (Table 3), it was found a decrease in surface area and an increase in pore diameter for this method.

In all the samples, the interplanar distance and the crystal size increase after the sorption, this is better appreciated in the sample irradiated by combined mode (Ac-mu). The shift to the left of the angle 2θ of the reflection (003) observed in Fig. 8, promotes an increase in the interplanar distance of 0.6 Å and in the crystal size of 2.9 nm, confirming that there was a greater degree of ionic exchange with the anionic species of the dye in the interlayer space of the HT and in the available sites, in comparison with the Ac-m and Ac-u samples (Paredes *et al.*, 2015).

As seen in Fig. 6, the area is independent of the sorption capacity when irradiating in combined mode (Ac-mu), more sites could be available (Al⁺³ in the brucite layer) to carry out the anion exchange more efficiently, which may be related to the decrease in the intensity of the signal corresponding to interlaminar water in the infrared spectrum of the Ac-mu sample (Fig. 7 b)) (Newman *et al.*, 1998; Bosch *et al.*, 2006; Paredes *et al.*, 2015; Zarazua 2018).

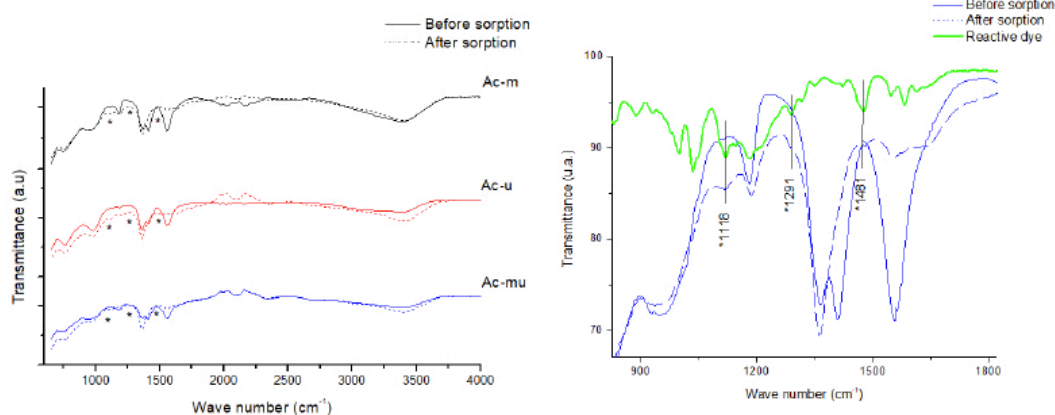
Fig. 7. Infrared spectra of a) HT-Al/Mg-CH₃COO samples Ac-m, Ac-u and Ac-mu; b) comparison of the infrared spectrum of the dye and the Ac-mu sample before and after the sorption.

Table 4. Interplanar distance (d) and crystal size (t) of HT-Al/Mg-CH₃COO synthesized. Before sorption After sorption

Sample	Before sorption		After sorption	
	Interplanar distance (d) (Å)	Crystal size (t) (nm)	Interplanar distance (d) (Å)	Crystal size (t) (nm)
Ac-m	7.6	5.6	7.7	6.8
Ac-u	7.4	5.6	7.5	5.6
Ac-mu	7.4	5.7	8	8.6

3.2.5 Transmission electron microscopy (TEM)

Fig. 9 shows TEM micrograph at 1000 000X, with a 100% image size increase in the insert of the figures of the Ac-m, Ac-u and Ac-mu samples a) before and b) after the reactive dye. Before the evaluation (Fig. 9 a)), planar defects can be observed in all cases. When irradiating with microwaves (Ac-m) a greater homogeneity is observed in the crystalline order according to the diffractogram by XRD (Fig. 8) with fewer planar defects. The sample irradiated with ultrasound (Ac-u) shows an increase in planar defects due to cavitation is observed. The Ac-mu sample has zones of preferential ordering similar to Ac-m sample but these zones are larger, corroborating that microwave irradiation predominates in the combine mode.

Fig. 9 b) corresponds to the compounds synthesized after the sorption of the reactive dye BEZAKTIV Red S-LF, the darker areas which are located in the 3 boxes (image increased by 100%) is the dye located in between the layers which confirms that it was anion exchange, although agglomerates are also observed due to the sorption of the dye in the available sites.

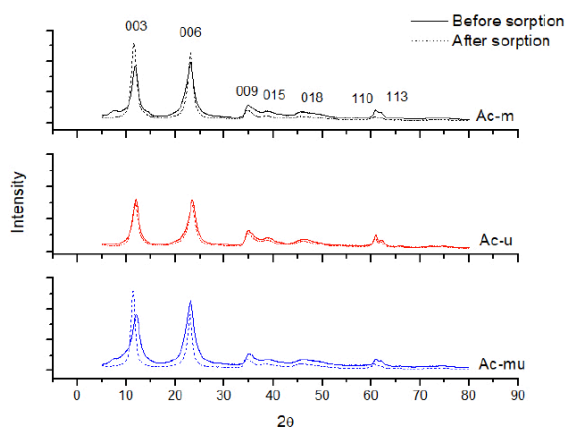


Fig. 8. Diffractograms of synthesized HT-Al/Mg-CH₃COO, before and after the sorption.

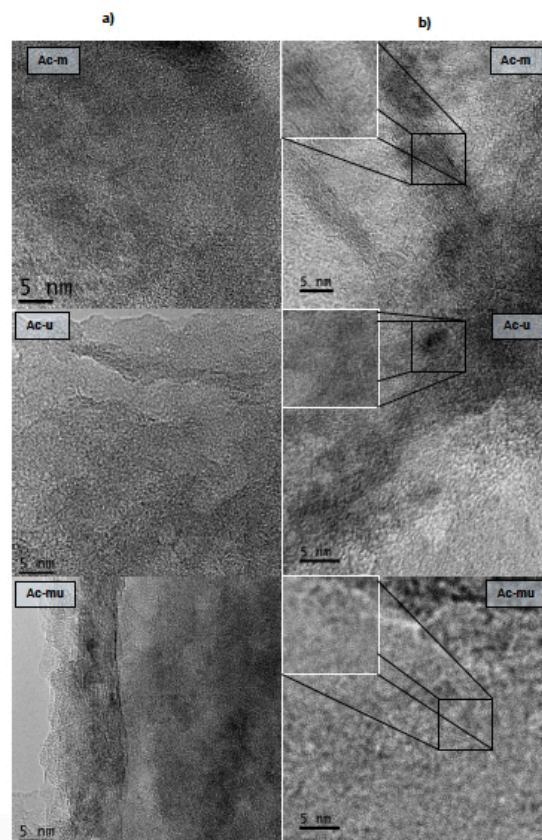


Fig. 9. TEM micrographs of the HT-Al/Mg-CH₃COO synthesized a) before and b) after sorption.

As the dye sorption does not depend on the surface area generated by the synthesis method, the sorption efficiency is attributed to the increase in the pore diameter and to the planar defects obtained by the combined irradiation mode (microwave-ultrasound), which left the Al³⁺ sites more exposed in the brucite layer, and this promoted an exchange of interlayer anions by the anionic species of the dye.

Conclusions

The amount of the dye absorbed depends on the method of irradiation used in the crystallization step. The maximum sorption capacity (q_{max}) of the dye depends on the characteristics obtained by the irradiation method used in the crystallization stage, where the compound irradiated in combined mode had the highest sorption capacity; and in all cases a physisorption was carried out based on the parameter n .

HT-Al/Mg-CH₃COO compounds were obtained with a laminar morphology independent of the method of irradiation in the crystallization step; by microwave irradiation a uniform morphology was obtained, while by ultrasonic irradiation a similar but more rugged morphology was presented due to the cavitation effect; when irradiated in a combined way (microwave-ultrasound) the morphology that predominates is that obtained by microwaves.

The mode of irradiation produces physical changes in the texture and crystallinity of the compounds, these characteristics depend on the mode of irradiation used in the crystallization stage, where the sample of greater surface area and pore volume was synthesized by ultrasonic irradiation (Ac-u) followed by the sample irradiated with microwaves (Ac-m) and in combined mode (Ac-mu); the Ac-m and Ac-mu samples have a similar and higher crystalline order than the Ac-u sample, because microwave irradiation predominates in the synthesis and the effect of this increases the crystallinity. By combining microwave-ultrasound irradiation, the active sites (Al⁺³ in the brucite-type layer) are exposed and allow an efficient exchange, increasing the sorption capacity in the Ac-mu sample.

The dye sorption does not depend on the surface area generated by the synthesis method and the sorption efficiency is attributed to the increase in the pore diameter and to the planar defects obtained by the combined irradiation mode (microwave-ultrasound), this has left more exposed the available Al⁺³ sites of the brucite layer promoting a better anionic interchange in comparison with Ac-m and Ac-u.

Acknowledgements

We thank the economical support for the projects SIP-20181871, SIP-20181207 and the institutes: Consejo Nacional de Ciencia y Tecnología (CONACyT), Centro de Nanociencias y Micro y Nanotecnologías (CNMN) and Instituto Politécnico Nacional (IPN).

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