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Modification of the Thermally Exfoliated Vermiculite by Sonication and Grafting Methods

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Abstract

In the present study, the thermally exfoliated vermiculite has been sonicated in order to grafting with the butyl-imidazolium. A suspension of vermiculite-water with 1% of concentration was sonicated at 20 KHz. This led to the decrease in the size of grains to16 μm after 2 h of treatment. Increasing of sonication time, presence of H_2O_2*, and the increase of the vermiculite concentration have caused an accentuation of sonication effect, this resulted the decreasing of the size to 10 μm. Moreover, a 2% fraction of submicron-sized particles was appeared. The pH of the vermiculite suspensions was increased. The number of the -OH sites was determined by acid-base titration using Gran method. The infrared spectra of the raw and sonicated vermiculites in* H_2O *or containing* H_2O_2 *were very similar. In the presence of* H_2O_2*, two bands were observed at 1380 and 1460* cm^{-1}*. These are due to the presence of carbonates anions formed during sonication in* H_2O_2*. XRD spectra showed that the sonication did not affect the vermiculite structure. The grafting was carried out on sonicated samples during 5 h in* H_2O*. This was realized in two steps. In the first step, we grafted 3-chloropropyltrimethoxysilane instead of the –OH sites. In the second step, we conducted a nucleophilic substitution of chlorine with methyl-imidazole. We proved by infrared spectroscopy and Gran method that grafting was real and XRD that this was not an intercalation.*

Keywords: clay, vermiculite, sonication, grafting, ionic liquids;

1. Introduction

Vermiculite is a layered phyllosilicate (type 2:1 or TOT), its sheet is an octahedral layer (type of Mg, Al, and Fe) sandwiched between two tetrahedral layers (type of Si and Al). Isomorphic substitution of Si^{4+} by Al^{3+} leads to the appearance of a negative charge at the sheet that will be compensated by hydrated exchangeable cations (Ca^{2+}, Mg^{2+}, Cu^{2+}, Na^{+}, K^{+}, H^{+}...) [1]. The adjacent sheets are attached by electrostatic forces and combinations of Van der Waals forces. Water molecules can be adsorbed in the interlayer space forming layers with interlayer cations, leading to swelling of the vermiculite. This adsorption depends on the hydrated cations state, which can be dehydrated, monohydrated or bihydrated, corresponding to the intercalation of 0, 1, or 2 plans of water molecules [2, 3].

The interaction of certain organic molecules with vermiculite may occur by adsorption, consequence of its large surface area or by intercalation consequence of swelling power of its interlayer space [4-6].

Vermiculite is also used for the adsorption of heavy metals [7-9]. These properties in addition to its environmental inertia make it a good candidate to be used in the water treatment field. Several scientific studies have been realised for the modification of vermiculite.

The most studied modification is the thermal exfoliation [10-18, 4]. Exfoliation improves certain properties of the vermiculite without diminishing its environmental inertia. This modification of the vermiculite causes a reduction of the apparent density and its thermal conductivity and an increase in its surface area and its melting point. Increasing the surface area of the vermiculite improves its adsorption capacity.

This improvement will be enhanced by decreasing the grains size by simple milling [6] or by sonication [19-26]. Mechanical milling is the simplest technique to reduce the grains size; it can be reduced to 40 μm [19]. However, aggressive milling can damage the vermiculite structure.The use of ultrasound seems to give better results [20].

They allow to obtain lower grains size without destroying the molecular structure of the clay.

Sonication in the presence of hydrogen peroxide for 10 hours can reduce the grains size of vermiculite to 15.5 μm. A size of 0.7μm was obtained after 80 hours of sonication [24]. A size of 1.7 μm was obtained after 25 minutes of sonication [27]. However, the increase of the sonication time can resulted aggregation of vermiculite [21, 23]. A finer grains size and higher surface area were obtained by "vibration milling, unfortunately this technique can leaded to the destruction of the vermiculite structure [28].

The sonication is the most appropriate method for obtaining nanoparticles without denaturation of physical or chemical properties of the material. The scattering of acoustic waves in the suspension of vermiculite-liquid (distilled water, hydrogen peroxide, alcohol … ..) until the imploding of formed bubbles generates Physical effects leading to fragmentation of the particles and producing smaller particles [29]. Generally, treatment with low-frequency ultrasound (20-100 kHz) has a physical effect on the adsorbents without changes in chemical structures. On the contrary high frequencies (>100 kHz) lead only to chemical effects.

Grafting vermiculite by specific chemical groups was also used to improve its water decontamination capabilities. The vermiculite has been grafted by manganese oxide [30]. Fernández et al grafted vermiculite by silane group [31]. This technique gives the best results when the limit to the modification by milling or sonication is achieved. Because generally, the grafting of clays wass carried out on the -OH groups located at the edges of the sheets. To increase the yield of grafting, it is essential to reduce the size grains of vermiculite and increase the number of -OH groups at the edges of the sheets.

In this study, we have investigated the effect of various parameters of sonication on the decrease of the thermally exfoliated vermiculite particles size. Knowing that ionic liquids have a special affinity with metals [32-37]. We grafted the smaller particles of vermiculite with butyl imidazolium to so as increase their capacity for adsorption of heavy metals.

2. Materials and methods

2.1. Clay

The studied vermiculite was provided by the CMMP (French company), originating from Yuli-China, (millimetric plates). Thermal exfoliation was achieved after a thermal shock in an oven at 600°C for 5 min. It was washed with deionized water several times. The insoluble impurities such as sand were precipitated and the exfoliated vermiculite floats on the water surface. After washing, the vermiculite is dried in an oven at 105°C for 12 h and was then milled to obtain a powder (denoted as: raw vermiculite). Its empirical formula is found to be: $(Si_3Al_1)(Mg_{2.62}Fe_{0.32}Ti_{0.06})O_{10}(OH)_2K_{0.45}Ca_{0.08}$ [38-39]. It has a cation exchange capacity of 148.6 meq/100 g.

2.2. Charactrisations

2.2.1. Infrared spectrophotometry

The samples were conditioned in a pellet form by compressing under 7 tons. 1.5 mg of sample was dispersed in 300 mg of potassium bromide. The infrared spectra were carried out between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} with 64 scans by a spectrophotometer Thermo Electron Corporation-Nicolet 380 FTIR spectrometer, brand.

2.2.2. Laser granulometry

Laser granulometry allows us to calculate the average size of the particles and determine the speciation percentage of each size. It is based on the diffraction of light according to the Fraunhofer theory. The used sail is MALVERN -INSTRUMENT brand, Mastersize type, S 32734-60 model. It allows the characterization of particles with diameters ranging from 0.02 to 2000 μm. The concentration of particles suspension must exceed 1 $g.L^{-1}$ so that the obscuration ratio will be satisfactory (about 9-10%). Before measurement the sample must be homogeneous in distilled water to ensure good dispersion. If the particles are agglomerated it is imperative to use an ultrasonic container for deagglomerated.

2.2.3. Acid-base titration

The acid-base titration allows us to quantify the -OH groups of clay, which will subsequently be used for grafting of butyl imidazolium. We have used the Gran method [41]. The experiment was carried out under argon atmosphere at 18°C. Clay-water suspension (1 g in 100 ml water UHQ) was firstly acidified at pH≈3 with hydrochloric acid (0.01 M). Then the basic titration was carried out with (NaOH 0.01 M) until the pH ≈ 10 [42, 43]. The concentration of electrolyte (NaCl) was adjusted to 1 $mol.L^{-1}$ to remove the exchange effects that can occur between the H^+ ions and the interlayer cations of the vermiculite. The representation of the function :

$$(V_0 + V_{at} + V_b).10^{-pH} = f(V_b)$$

$$(V_0 + V_{at} + V_b).10^{+pH} = f(V_b)$$

for acid side and for the basic side, (V_0 is the volume of clay suspension, V_{at} is the volume of added acid to achieve a pH around 3 and V_b is the volume of added base) allowed us to determine the equivalent points V_{eb1} and V_{eb2} (V_{eb1} is equivalent to OH^- ions that neutralize the excess of H^+ ions in the suspension and $V_{eb2} - V_{eb1}$ is equivalent to OH^- ions which react with acceptor sites of clay) using extrapolations on the two branches of the curve Gran. The concentration of surface sites (CSSA) was calculated by the following formula:

$$CSSA(mmol.L^{-1}) = \frac{[(V_{eb2} - V_{eb1})_{sample} - (V_{eb2} - V_{eb1})_{blank}] \times C_b}{V_0}$$

The number of active sites (NSA) was deducted from the above formula by divided the number of moles of active sites surface (V_0xCSSA) to the mass of the clay (1g) in the suspension. Sites active number was given by following equation:

$$NSA(mmol.g^{-1}) = [(V_{eb2} - V_{eb1})_{sample} - (V_{eb2} - V_{eb1})_{blank}] \times C_b$$

The representations of Gran (below) are plotted as function of V_b. Therefore, the second branch of acid-base titration which was used (passage of acid pH to basic pH). We have performed the acid-base titration for the blank (100 ml of 1M NaCl solution), where: $V_{eb1\ blank}$=2.3 ml and $V_{eb2\ blank}$ = 5.7 ml (Figure 3.(a))

2.2.4. X-ray diffraction (XRD)

The XRD analyses were performed in a Bragg-Brentano geometry using a Brukers D8 Advance diffractometer (acceleration voltage of 40 kV and an electron current of 30 mA) equipped with a Ge monochromator and using the Cu $k_{\alpha 1}$ incident radiation (λ=1,5406 nm).

2.2.5. pH of vermiculite-solvent suspensions

The pH of clay-solvent (H_2O or H_2O_2) was measured using a pH meter (NF ISO 10390, 2005) before and after the sonication. The pH measurement was performed after the preparation of clay suspension in water or hydrogen peroxide at a ratio of 1/5 (v/v).

2.3. Ultrasonic treatment

The raw vermiculite was sonicated in aqueous solution either in presence or absence of hydrogen peroxide (concentration of 35%). The used reactor for the sonication is a glass reactor 60 ml of volume. It is a cylinder at double-walled which allowed us to maintain the suspension at 25°C during sonication. Ultrasound is generated by a generator Sonics and Materials 500W Ultrasonic Processor-VC505. The used titanium probe has a diameter of 13 mm and was immersed to a 1.5 cm in the suspension. The frequency of sonication was 20 KHz and the power was set at 70% of 500 W that can produced by the generator. The concentration of the vermiculite in aqueous solution either in presence or absence of hydrogen peroxide was set at 1 and 7%. The time of sonication was set at 2 and 5 h. After treatment, the obtained samples were dried at 80°C for 48 h.

The calorimetric method was applied to determinate the acoustic power of our system. A thermocouple was immersed in distilled water to control the increase in temperature during the sonication (for a few minutes (3 min) without cooling) in the cylindrical reactor. The values of (t, T) were: (0, 295.5), (30, 303.95), (60, 312.05), (90, 320.35), (120, 326.65), (150, 333.15), (180, 339.05), where: t is the sonication time (s) and T is the temperature of our system (K). The acoustic power was calculated using the following equation [40]:

$$U_p = m.C_p.\frac{dT}{dt}$$

Where C_p is the heat capacity of solvent at a constant pressure ($J.kg^{-1}.K^{-1}$), m is the solvent mass (kg) and $\frac{dT}{dt}$ ($K.s^{-1}$) is the rate of temperature increase. A 56 W acoustic power was found for our system.

2.4. Grafting procedure

The grafting was carried out on sonicated vermiculite sample in H_2O at 7% of concentration for 5 h (denoted as V: H_2O, 5 h). Before grafting, the sample was dried with nitrogen liquid for 3 h and introduced overnight in a desiccator. The used reagents (methyl-imidazole, acetonetrile, toluene, and 3-chloropropyltrimethoxysilane 3-CPTMS) for grafting have a purity of 99% and originating from Sigma Aldrich. The grafting was carried out in two steps. At the first step, we grafted the 3-chloropropyltrimethoxysilane (3-CPTMS) on the edge surface of the vermiculite sheets *(Figure .1)*.

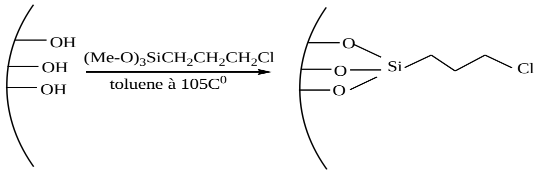

Figure 1: Schematic illustration of the procedure of the first grafting step.

During the second step, we have carried out a nucleophilic substitution of chlorine with methyl-imidazole *(*Figure .2*)*.

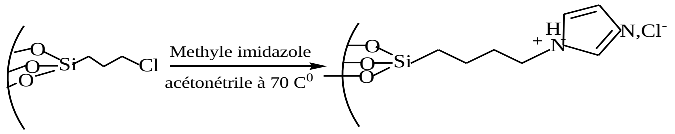

Figure 2: Schematic illustration of the procedure of the second grafting step.

During the first step, an amount of 10 g of sample was introduced into 50 ml of dry toluene with an excess of 3-CPTMS in a three-necked flask. The system was kept under reflux system at 105°C under argon atmosphere for 6 h. The obtained product (denoted as V-CPTMS) was filtered under vacuum, washed six times with a water-acetonitrile mixture and dried with liquid nitrogen and placed in a desiccator. This step allowed making the substitution of -OH of vermiculite edges by 3-CPTMS. For the second step of grafting, we introduced the product of the previous reaction (V-CPTMS) with 40 ml of dry acetonitrile and excess of methyl-imidazole (4 ml) in a three-necked flask. The system was stirring under reflux system at 70°C for 48 h. The obtained product was filtered, washed 6 times with distilled water and dried at 80°C for 48 h (denoted as V-CPTMS-Me.Im). This step has achieved the nucleophilic substitution of chlorine with methyl-imidazole.

3. Results and discussion

3.1. Modification by ultrasonic irradiation

3.1.1. Measurements of pH

The pH measurements of vermiculite suspensions in water either in presence or absence of hydrogen peroxide were performed before and after sonication. The obtained results are summarized in the table 1. The effect of ultrasound on the pH of vermiculite suspension depends on the sonication time and is depreciated with time. The sonication of the vermiculite in water either in presence or absence of hydrogen peroxide leads to the dissolution of the interlayer cations (Ca^{2+} and K^+) in the solution. The water molecules located on the clay surface dissociate into OH^- and H^+ ions. OH^- ions were released into the solution to keep the electrical equilibrium while H^+ ions were captured by -OH groups of clay surface or intercalated in the interlayer space. The excess of OH^- ions in solution has leaded to the increase of pH [44]. Muromtsev et al [45] noted the expulsion of interfoliares exchangeable ions (Mg^{2+} and Ca^{2+}) in aqueous solution by exfoliated vermiculite, in addition, the appearance of OH^- ions to keep electrical equilibrium. These ions react with carbon dioxide dissolved in solution during sonication to form carbonate anions CO_3^{2-}.This reaction is evidenced by infrared characterization of the sonicated vermiculite (*Figure 4.).* The pH of vermiculite-water suspensions either in presence or absence of hydrogen peroxide was increased with respect time, but this increase was greater in the presence of hydrogen peroxide. This is explained by the decomposition of hydrogen peroxide, which increases the concentration of OH^- anions during sonication (in addition to those released by the clay). Increasing the concentration of vermiculite from 1% to 7% decreases the effect of ultrasound on the pH. In fact, this increase has leaded to an increase in the viscosity of the suspension which has interfered cavitation effects.

Table 1: pH of the solvent-vermiculite suspensions before and after the ultrasonic irradiation.

Concentration of clay	1%			7%		
Time of sonication (h)	0	2	5	0	2	5
pH of H_2O-clay suspensions	9	9.5	9.6	9.4	9.7	9.84
pH of H_2O_2-clay suspensions	3.4	5.36	-----	5.7	6.27	6.34

3.1.2. Acid-base titration

The number of -OH sites located on the edges of the vermiculite sheets were determined by acid-base titration using the Gran method. Based on the acid-base determination method that was mentioned above, we can plot the Gran curves, which allow determining the number of –OH sites. After linearization, we found that V_{eb1}=3.9 ml and V_{eb2}=8.3 ml for the raw vermiculite (*Figure 3.(b)*).Using the following relation:

$$NSA = \left[(V_{eb2} - V_{eb1})_{sample} - (V_{eb2} - V_{eb1})_{blank}\right] \times C_b = 0.010\ mmol.g^{-1}$$

WhereV_{eb2} and V_{eb1} of blank were measured previously (*Figure 3.(a)*). For sonicated sample during 5h in the presence of peroxide hydrogen (*Figure 3.(c)*), we found that V_{eb1}=16 ml, and V_{eb2}=27 ml. NSA=0.076 mmol.g^{-1} (*Table 2*). The number of active sites (-OH) of the raw vermiculite was 0.010 mmol.g^{-1}. After ultrasonic irradiation, the value of NSA was clearly increased. After 5 h of sonication in H_2O_2 media, it was reached at 0.076 mmol.g^{-1}, which that represents 7.6 times of the raw clay. This increase was a consequence of the perpendicular rupture of the clay layers, resulting -OH groups on the edges of the new smaller particles.

Table 2: The values of V_{eb1},V_{eb2}, CSSA and NSA for raw vermiculite, V: H_2O_2, 5 h and V-CPTMS samples.

Clay	Raw vermiculite	V: H_2O_2, 5h	V-CPTMS
V_{eb1} (ml)	3.9	16	2.1
V_{eb2} (ml)	8.3	27	5.8
NSA (mmol.g^{-1})	0.01	0.076	0
CSSA (mmol.L^{-1})	0.1	0.76	0

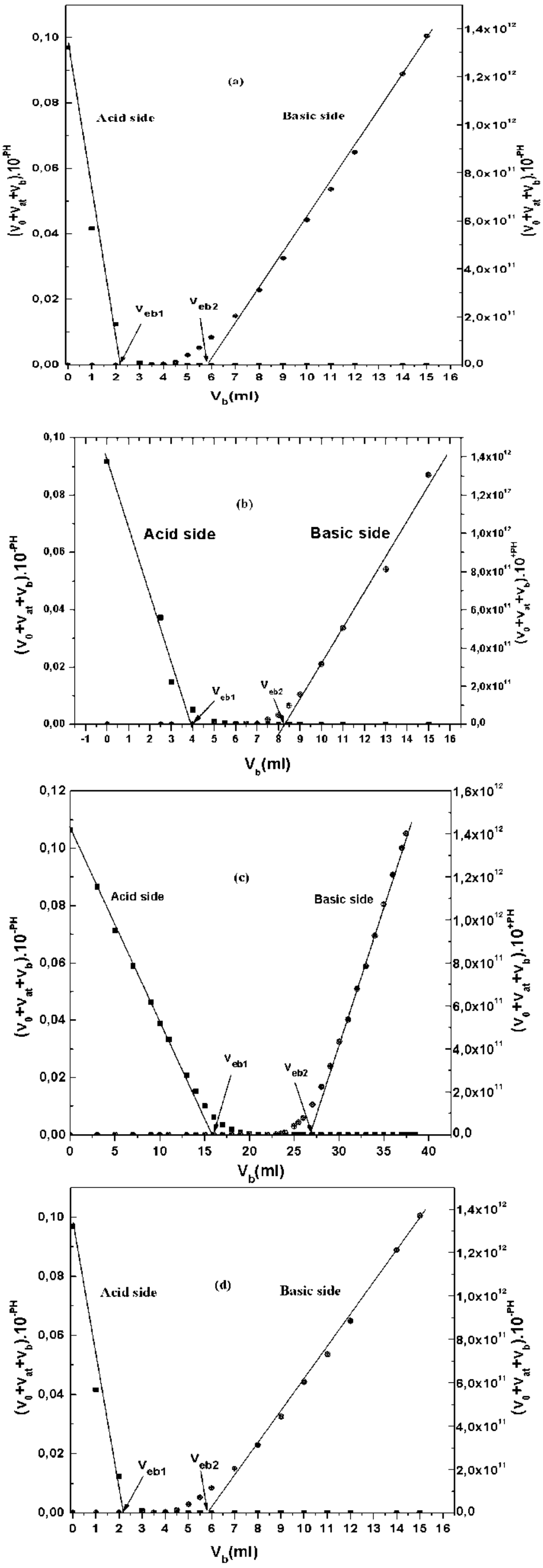

Figure 3: Curve Gran of: (a) blank (0.1 M NaCl), (b) raw vermiculite, (c) V: H_2O, 5 h and (d) V-CPTMS .

3.1.3. Infrared spectra

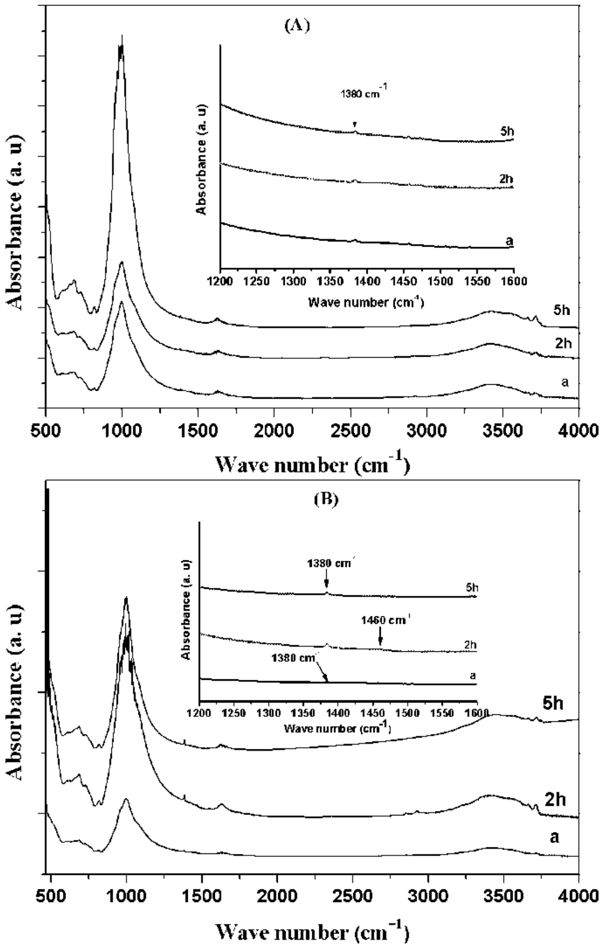

Figure 4: Infrared spectra of the clays: (A) raw vermiculite -a- and its sonicated samples in water after 2 h and 5 h, (B) raw vermiculite -a- and its sonicated samples in hydrogen peroxide after 2 h, and 5 h.

Figure 4. show the infrared spectra of the raw and sonicated vermiculites samples in water (a) and in water containing hydrogen peroxide at 7% of concentration (b), it can be seen that the results were very similar. This indicates that no structural change of the sheets during the irradiation. The broad band at 1000 cm^{-1} was attributed to the stretching vibration of the group (Si-O). The two broad bands at 450 cm^{-1} and 686 cm^{-1} were attributed to the stretching vibration of the group (Al-O) [46]. The broad vibrational band of water at 3430 cm^{-1} was assigned to the asymmetric and symmetric stretching vibrations of the group -OH. The two bands at 3660 cm^{-1} and 3720 cm^{-1} were assigned to the stretching vibration of the -OH groups of the sheets. The frequency at 3660 cm^{-1} was assigned to the stretching vibrations of -OH groups in $Mg(OH)_3$ tetrahedron of the vermiculite [46, 47]. For sonicated vermiculites in water containing hydrogen peroxide, two bands were observed, the first was intense and narrow at about 1380 cm^{-1} while the second was broad at about 1460 cm^{-1} (*Figure 4.(B)*). They were assigned to the presence of carbonates ions formed by the dissolution of carbon dioxide of the air with the hydroxide ions (OH^-) released by the clay [48] and those generated by the decomposition of hydrogen peroxide. We also noted that there was a small amount of carbonates in the raw vermiculite (*Figure 4.(B)*), (The peak was less intense compared to the sonicated samples for 2 and 5 h). This amount was increased after sonication. The carbonates ions CO_3^{2-} were formed during the sonication, which were generated by the reaction of carbon dioxide of the air with the hydroxide ions (OH^-). The ultrasounds also induce to the decomposition of the hydrogen peroxide leading to an increase of the amount of OH^- ions in the solution. The OH^- ions in the solution were the result of the decomposition of hydrogen peroxide and the (OH^-) ions released by the vermiculite. These two sources of OH^- lead to the increase in amount of dissolved carbon dioxide in the suspension, and this according to the reaction:

$$CO_{2(aq)} + 2OH^-_{(aq)} \rightarrow CO^{2-}_{3(aq)} + H_2O_{(l)}$$

The formed carbonates react with the interlayer ions to form K_2CO_3 and $CaCO_3$ salts.

$$2K^+_{(aq)} + CO^{2-}_{3(aq)} \rightarrow K_2CO_{3(aq)}$$

$$2Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow CaCO_{3(aq)}$$

For the sonication in water, there is a single source, OH^- ions released by the clay leading to the reduction in the quantity of dissolved CO_2 gas during the sonication , that is why the intensity of the peak around 1380 cm^{-1} is lower than that observed with hydrogen peroxide (*Figure 4.(B)*).

3.1.4. Granulometric curves

Before sonication, the granulometric curve of the raw vermiculite showed a single peak (Figure 5.), the average particles size was 80 µm (the maximum of peak position), the full width at half maximum (FWHM) of the peak was 220 µm, the percentage volume was 9% and all the particles located in the range of 2-800 µm. Firstly, we have sonicated a 1% vermiculite solution. After 2 h of sonication, a peak at 16 µm was appeared with a FWHM of 35 µm and a volume percentage of 11.3%, the particles size was in the range of 1-110 µm. There is also a small peak located in the range of 0.5-1 µm was appeared, which is related to submicron-sized particles and which has a percentage of 0.8%. After 5 hours of sonication, a peak at 12.2 µm, with a FWHM of 20 µm and a volume percentage of 11.6%, was appeared, the particles were in the range of 1-44 µm and the percentage of the submicron-sized particles was increased to 1.6%. The sonication effect is interpreted by the effectiveness of the physical effects of ultrasound caused by acoustic cavitation leading to the fragmentation of vermiculite particles. In the presence of hydrogen peroxide, after two hours of sonication, a peak at 15 µm was appeared with a FWHM of 25 µm and 12% of volume percentage, the particles was in the range of 1-80 µm and the percentage of the submicron-sized particles was 1%. The sonication leads to a reduction of the grains size.

This decrease is accentuated by the presence of hydrogen peroxide in solution during treatment. This is the result of the decomposition of hydrogen peroxide which generates oxygen gaz that produces a pressure between the sheets and thus break the vermiculite particles. This phenomenon was very clearly at low concentration of clay. Secondly, we have increased the vermiculite concentration to 7% in order to increase the yield of low particles size. In this case, after 2 hours of ultrasonic treatment in the absence of hydrogen peroxide, the average grains size has decreased, and the maximum of the peak correspond the particles size distribution curve is located at 16 µm, the particles were in the range 1-60 µm, the percentage volume was 13% and the percentage volume of submicron-sized particles was 0.8%. After 5 hours of treatment, the maximum of the peak of the grains size distribution curve is decreased to 10 µm, the particles were in the range 1-40 µm with 11% of percentage volume and the percentage volume of submicron-sized particles was 2%. The presence of hydrogen peroxide does not improve the efficiency of the sonication at this concentration. Indeed, the maximum of the peak of the size distribution curve was 16 µm after 2 hours of treatment and it was 12 µm after 5 hours of treatment. The particles were in the range of 1-63 µm for 2 hours and in the range of 1-40 µm for 5 hours of treatment. The submicron-sized particles were in the range 0.5-1 µm and the volume percentage of these particles was 0.8% and 2% for 2 hours and 5 hours of treatment, respectively. Increasing the vermiculite concentration reinforces ultrasonic effects on particles size. This is due to the increase of collision probability between the vermiculite particles. This result was observed by Michael [49], for the ultrasonic treatment of the alumina in aqueous solution. Granulometric curves showed that the ultrasound efficiency is important at the beginning of treatment and this in either the presence or absence of hydrogen peroxide. The treatment time is important for the obtained amount of submicron-sized particles.

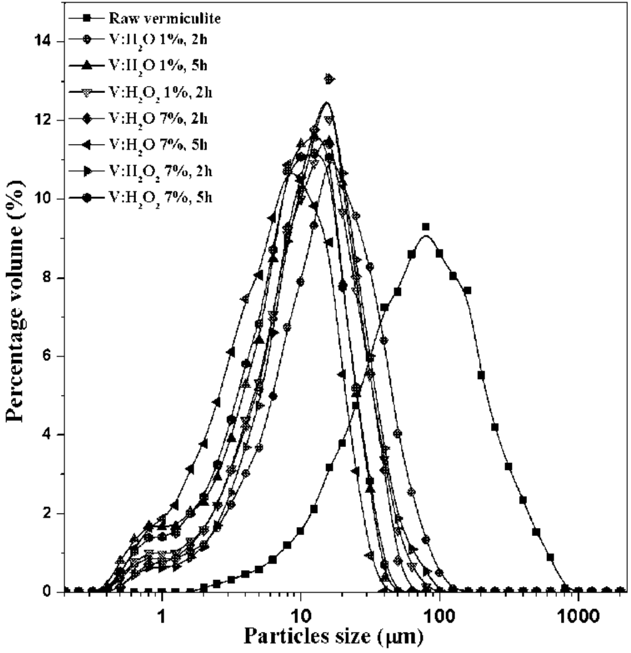

Figure 5: Granulometric curves of the raw and sonicated vermiculites.

3.1.5. X-ray diffraction (XRD)

We performed the XRD spectra of the raw vermiculite and sonicated samples at 7% of concentration either in presence and absence of hydrogen peroxide (*Figure 6*.). This was in order to determine the sonication effect on the grains structure. The basal spacing is modified by the presence of hydration water molecules. This results in the change of the peaks position in the XRD spectra. Studied Vermiculite contains two cations in its interlayer space: potassium K^+ and calcium Ca^{2+}. Potassium being dehydrated while calcium is intercaled with a monolayer water [2, 3]. The narrow and more intense peak in spectra (identified as (002a)) which is located at 2θ=6.04° corresponds to a basal spacing d=14.60 Å (interfoliare space) [12, 18, 50]. Another narrow and intense peak (identified as (002e)) located at 2θ=8.84° corresponds to a basal spacing d=10.0 Å, this spacing contains the dehydrated K^+ ions. This peak is the only one which stayed on the XRD spectra when vermiculite was exchanged by K^+ ions (*Figure 6*.). The peak identified as (002b) located at 2θ=7.02° corresponds to a basal spacing d=12.57 Å, where is containing the monohydrated Ca^{2+} ions. The other peaks (identified as (002c) and (002d)) located at 2θ=7.40° and 2θ=8° correspond respectively to basal spacing d=11.93 Å and d=11.04 Å were the result of interbedded layers containing K^+ and Ca^{2+} ions. The sonication of the vermiculite in water leaded to decrease in the intensity and broadening of the peak (002a). This effect was more pronounced with time. After sonication of the vermiculite in water during 2 hours, the peak intensity related to (002a) reflection was greatly decreased which results in enlargement of the FWHM of the peak that was ω=0.0021 rad and becomes 0.0031 rad. After 5 hours of sonication, the peak intensity was more decreased and FWHM was more increased and becomes 0.0054 rad. The other peaks associated to (002b), (002c) and (002d) reflections were also decreased after two hours of sonication. After 5 hours of sonication, the intensity of these peaks was more reduced. The intensity of the peak related (002e) reflexion was also more reduced with time. Generally no destruction of the crystal structure has been noted. But the average of crystallites size was decreased after the sonication. We can calculate the average crystallites size according to –c- axis using the Debye-Scherrer's equation:

$$a = \frac{0.9\lambda}{\omega.\cos\theta}$$

((002a) reflexion at 2θ=6.04°). Where: a is the average crystallites size (nm), λ is the X-ray wavelength (0.15406 nm for Cu $K\alpha_1$), ω is the FWHM of the peak (radians) and θ is the angle diffraction (deg.). Therefore, the size of the raw vermiculite was about of 67 nm; it became 45 nm after 2 hours and reached to 31 nm after 5 hours of sonication. This reduction can be explained by the fragmentation of grains and desorption of interfoliares cations in the solution. Concerning the sonicated samples in the presence of hydrogen peroxide, the same remarks were observed, but the crystallites size were more reduced; therefore, after 2 hours of sonication became 36 nm and reached to 27 nm after 5 hours of sonication (*Table 3*.). So, the ultrasound at 20 KHz has a breaking effect of vermiculite particles in water suspension either in presence or absence of hydrogen peroxide due to acoustic cavitation. We can say that the ultrasound at this frequency has only a mechanical effect.

Table 3. The values of the crystallites sizes of the raw and sonicated vermiculite.

Solvent	H_2O			H_2O_2		
Time of sonication (h)	0	2	5	0	2	5
Average crystallites size according to -c- axis (nm)	67.5	45	31.5	67.5	36	27

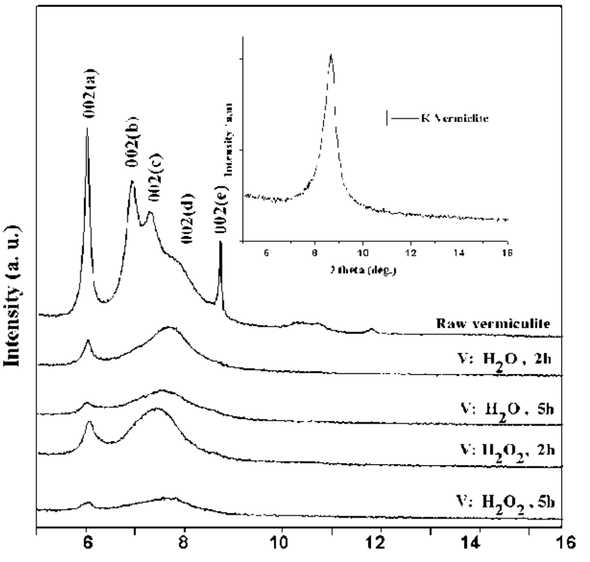

Figure 6. XRD spectra of the raw vermiculite and sonicated samples in aqueous solution in absence and presence of hydrogen peroxide.

3.2. The grafting modification

The sonication of vermiculite allowed us to reduce its grains size and thus increase the number of -OH sites which will be grafted. The mixture of the vermiculite with 3-CPTMS under inert atmosphere has allowed to grafting -OH groups with later. The obtained sample (V-CPTMS) was washed to eliminate the rest of the 3-CPTMS which can be intercaled or adsorbed. After that, the obtained sample was reacted with an excess of methyl-imidazole to have a substitution of the latter instead of chlorine. Then, we washed the grafted sample (V-CPTMS-Me.Im) to get rid of any intercaled or adsorbed methyl-imidazole. The infrared spectra of the initial and grafted samples were shown in *Figure 7.*

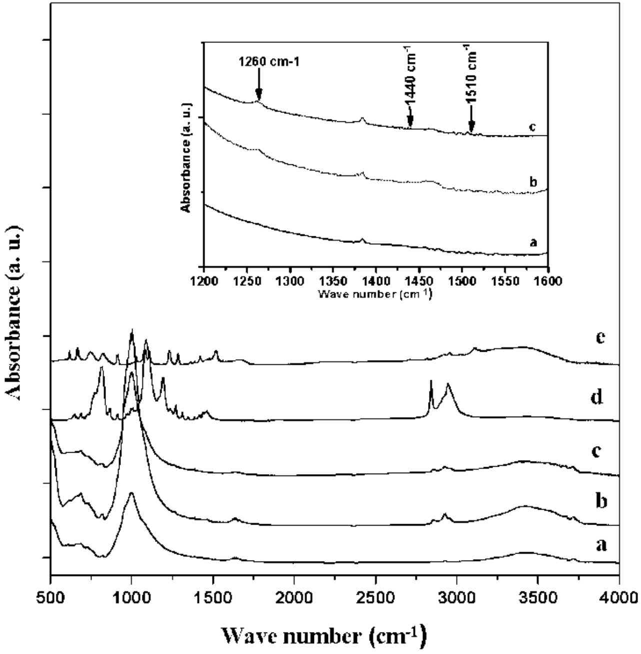

Figure 7: FTIR spectra of the sonicated vermiculite in H_2O for 5 h and grafted vermiculite: V: H_2O_2, 5 h (a), V-CPTMS (b) ,V-CPTMS-Me.Im (c), 3-CPTMS (d) and methyl imidazole (e).

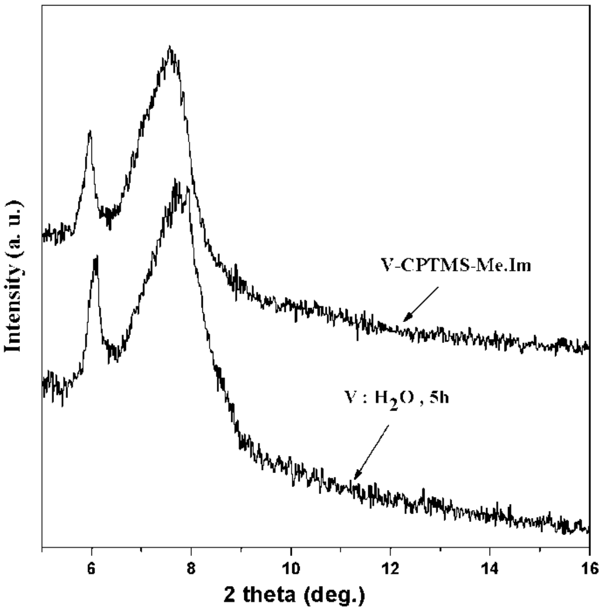

Figure 8: XRD spectra of the grafted and sonicated vermiculite in H_2O for 5 h.

The similar bands on the spectra of the samples a,b and c were: The broad band between 3200 cm^{-1} and 3600 cm^{-1} was assigned to the asymmetric and symmetric stretching vibrations of the group -OH of water (υ_{O-H}). The band around of 1600 cm^{-1} was a binding of the physosorbed water on clay (δ_{O-H}). The broad band at 1000 cm^{-1} was assigned to the Si-O group (υ_{Si-O}). The two broad bands at 450 cm^{-1} and 686 cm^{-1} were attributed to Al-O group (υ_{Al-O}). The narrow band around 1380 cm^{-1} was attributed to a quantity of carbonate ions formed by dissolving carbon dioxide gas during sonication. New peaks were appeared on the spectra (b). The first three were about 2860 cm^{-1}, 2930 cm^{-1}, 2960 cm^{-1}. These peaks were assigned to stretching vibration symmetric and asymmetric of (C-H) group due to the presence of propyl group of CPTMS [$Cl-CH_2-CH_2-CH_2-Si(O-CH_3)_3$] and at 1410 cm^{-1} for $-CH_2-$ bending [51] . Another peak due to stretching vibration of Si-O-Si group was appeared at around 1260 cm^{-1}. This proved that CPTMS was grafted onto vermiculite. On the spectra (c), low peak at 3250 cm^{-1} was observed, it was assigned to the stretching vibration of N-H group of imidazole (υ_{N-H}). Other bands of imidazole were very weak. We performed a zoom on the part of spectra ranging between 1200 and 1600 cm^{-1} to be able to see the *Figure 7.* Two peaks were appeared at around 1510 cm^{-1} and 1440 cm^{-1}. They were assigned to the stretching vibrations of C=C and C=N groups, respectively. This proved that the methyl imidazole was grafted onto vermiculite. We vigorously washed the grafted sample to eliminate intercalated or adsorbed methyl imidazole onto vermiculite, and we proved by XRD spectra that no intercaled molecule during grafting was observed. The XRD spectra of the vermiculite before and after grafting were represented in the *Figure 8.* There was an attenuation of the peak intensity and no shift of its position was observed. This removed any risk of new intercalation during grafting. The decrease of the peak intensity after grafting is a frequently observed phenomenon [31, 52]. We also plotted the Gran curve of the V-CPTMS sample

(Figure 3.(d)). After linearization, we found that V_{eb1}=2.1 ml and V_{eb2}=5.8 ml, so $NSA \approx 0\, mmol.g^{-1}$ (*Table 2.*), we proved that all -OH sites of initial vermiculite were replaced by CPTMS.

4. Conclusion

In this work, we have studied the effect of ultrasound on the thermally exfoliated vermiculite in order to grafting with butyl imidazolium. The raw and modified vermiculites were characterized by laser granulometry, X-ray diffraction, infrared spectrophotometry, measurements of pH of suspensions and acid-base titration. The sonication was performed in aqueous solution with a clay concentration of 1% and 7%. Then, we have studied the effect of the presence of hydrogen peroxide in aqueous solution on the ultrasound efficiency. The clay concentration has been increased from 1 to 7% in order to increase the sonication efficiency. Our study has shown that the effect of ultrasound on the size of the vermiculite particles was important in beginning of sonication, it was decreased with time. The average grains size of vermiculite was achieved to 10 µm after five hours of sonication with appearance a small fraction of submicron-sized particles. The fragmentation of the clay particles leaded to increasing of clay suspensions pH and the number of -OH groups located on the edges of the clay sheets. This fragmentation was accentuated with increasing of the sonication time, increasing of clay concentration and the presence of hydrogen peroxide. The infrared and XRD spectra showed that no structural change of the vermiculite after sonication. Infrared spectra of the raw and sonicated vermiculite were very similar, the exception of the appearance of a peak at around 1380 cm^{-1} which showed the formation of carbonates ions (CO_3^{2-}) during sonication of vermiculite in the presence of hydrogen peroxide. XRD spectra showed the decrease of the vermiculite crystallites size. The grafting of butyl imidazolium was performed on Vermiculite sample having the smallest grains size; it was carried out in two steps. Firstly, we grafted 3-chloropropyltrimethoxysilane (CPTMS-3) on the edge surface of the vermiculite sheets. Then, we carried out a nucleophilic substitution with methyl imidazole. We have proved by infrared spectroscopy and Gran method that the grafting is real and XRD that this is not an intercalation.

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