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# Microwave assisted acid treatment of sepiolite: The role of composition and "crystallinity"

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# ABSTRACT

Three sepiolites with differences in composition and structural ordering were treated with 0.2 N HCl and 0.2 N  $HNO_3$  solutions assisted with microwave radiation. This treatment caused in the firsts 16 min the progressive  $Mg^{2+}$  depletion of the octahedral sheet, the gradual degradation of the sepiolite structure and the formation of an amorphous silica phase which contributes to a noticeable increase of the BET specific surface area. The assistance of microwaves during the acid treatment allows us to get specific surface areas equivalent to those obtained after 48 h with conventional heating methods. The influence of mineralogical impurities, "crystallinity" and chemical composition on the reactivity of sepiolite were also studied.

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### 1. Introduction

Sepiolite is classified as having a modulated structure because of the inverted tetrahedral arrangement and the formation of the channel where the octahedral sheet becomes discontinuous (Guggenheim and Eggleton, 1987, 1988). This particular structure results in development of structural channels and a typical fibrous morphology which are the main reason for the characteristic properties of this clay mineral (Guggenheim and Krekeler, 2011; Ruiz-Hitzky et al., 2011, and references therein). The structural formula of sepiolite is Si<sub>12</sub>O<sub>30</sub>Mg<sub>8</sub> (OH)<sub>4</sub>(OH<sub>2</sub>)<sub>4</sub>.nH<sub>2</sub>O (Brauner and Preisinger, 1956), where the four possible octahedral positions are occupied by Mg. Although sepiolite is an almost pure magnesian clay mineral, the existence of structural substitutions of Mg in the octahedral sheet by Al and Fe has been reported (García-Romero and Suárez, 2010; Suárez and García-Romero, 2011).

Because of its structural features, sepiolite has received considerable attention with regard to the adsorption of organics on the particle surfaces (Akyüz et al., 1995) and to its use as support for catalysts (Corma et al., 1988; Occelli et al., 1992). The presence of channels in its structure allows the adsorption of  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$  and  $Pb^{2+}$ , giving rise to important environmental applications (Álvarez-Ayuso and García-Sánchez, 2003; Brigatti et al., 1996, 2000; Kara et al., 2003; Vico, 2003).

In particular, acid treatments have been classically used to increase the surface area and to obtain solids with high porosity and a high number of acidic centers from this clay mineral (Jiménez-López et al., 1978). During acid treatments of sepiolite, variable amounts of structural  $Mg^{2+}$ ions are removed, depending on the intensity of the acid treatment. If the treatment was aggressive enough, the octahedral cations are dissolved while the tetrahedral sheets form free amorphous silica gel. insoluble in the acid solution. In this sense, Corma et al. (1986) found that the removal of  $Mg^{2+}$  and  $Fe^{2+}$  is easier than  $Al^{3+}$  because the last usually occupies the center of the ribbons and hence is more difficult to remove. However, the crystal lattice of sepiolite is not entirely disrupted despite the acid treatment. The correlation between the quantity of Mg<sup>2+</sup> ions released from sepiolite and its properties, mainly an increase of the surface area (Aznar et al., 1996; Inukai et al., 1994) and the ability for adsorption on acid-activated sepiolite, have been reported in several studies (Kara et al., 2003; Sabah et al., 2002; Vico, 2003). The microporous channels are considerably altered with this treat-

In order to improve the adsorption capacity of sepiolite various surface modification methods (activation) such as heat and acid treatment

have been studied by many researchers (Balci, 1996; Dekany et al.,

1999; González-Pradas et al., 2005; Kara et al., 2003; Tan et al., 2004).

ment, producing a sensible change in the porosity of sepiolite. Indeed the acid treatment modifies the number of acid sites by disaggregation of particles, elimination of mineral impurities, removal of metalexchange cations and proton exchange (Myriam et al., 1998). Therefore, it is possible to enhance the adsorption properties of sepiolite using the appropriate treatment. Jiménez-López et al. (1978) studied the evolution



Research paper





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Fig. 1. Band component analysis of the XRD patterns of starting sepiolites.

of surface area in sepiolite as a function of acid and heat treatment. Acid activation of sepiolite was carried out with boiling solutions of HNO<sub>3</sub> (with concentration ranging from 1 to 5 N) for 1 h, the resulting samples were heat treated (from 110 to 900 °C) for 100 h. The maximum increases of surface area (from 336 to 391 m<sup>2</sup>/g) were reached with 1 N HNO<sub>3</sub> solution and heating at 300 °C. In this sense, Vicente Rodríguez et al. (1994) found a parallel increase in specific surface area and acid sites with the acid treatments. They obtained the maximum values of surface area with 2.5% HCl for samples treated for 24 h (from 293 to 492 m<sup>2</sup>/g) and with 1.25% HCl after 48 h (from 293 to 549 m<sup>2</sup>/g).

Microwave techniques for heating are currently used in many chemical processes (Banković et al., 2013; Tyagi et al., 2006; Vicente et al., 2011). The use of microwave-heating techniques in the activation of clay minerals offers advantages over conventional methods including a higher heating rate that reduces the treatment time and provides homogeneous heating. Considering, the importance of "crystallinity" on the surface area (Pozo et al., 2014), in this work we report the influence of the microwave-assisted acid treatment on the structure and texture of three samples of sepiolite with different compositions and crystalline ordering.

## 2. Experimental

#### 2.1. Starting material and microwave acid assisted treatment

Three samples of sepiolite with differences in composition and structural ordering were selected for this study, named S1 (Vicálvaro), S2 (Barajas) and S3 (Batallones) all of them from the Madrid Basin deposits (Spain). Exactly, 5 g of dried sepiolite was treated with 50 ml of 0.2 N HCl or HNO<sub>3</sub> for 2, 4, 8 and 16 min under microwave radiation at 800 W, in an open glass cylinder reactor. After treatment the solids were dried at 80 °C for 48 h and then the dried samples were weighed on a precision weighing balance. The starting sepiolites and resulting materials were characterized by X-ray diffraction, X-ray fluorescence, FTIR spectroscopy, nitrogen adsorption–desorption and scanning electron microscopy.

## 2.2. Microwave system

A commercially available microwave system EMS201000X (Electrolux, Stockholm, Sweden) operating at 800 W and 2.45 GHz was used for treatments. Following Korichi et al. (2009), to avoid exceeding 100 °C in the system, the microwave irradiation was applied

in a discontinuous form. After 1 min of microwave irradiation the suspensions were cooled for 5 min at room temperature.

After microwave-assisted acid treatment, the samples were centrifuged and washed with deionized water until the complete elimination of  $NO_3^-$  or  $Cl^-$  ions, tested through Griess and AgNO<sub>3</sub> tests respectively, and finally, were air- dried.

#### 2.3. Characterization

Powder patterns for the samples were collected on an X'Pert Pro MPD automated diffractometer (PANalytical B.V.) equipped with a Ge(111) primary monochromator (strictly monochromatic CuK $\alpha$ 1 radiation) and an X'Celerator detector. The overall measurement time was 33 min per pattern to have very good statistics over the 2 $\theta$  range of 2–65° with 0.017° step size.

The chemical analysis (major elements) of untreated samples and obtained products was performed by means of the MagiX X-ray fluores-cence (XRF) spectrometer of PANanytical.

Nitrogen adsorption–desorption isotherms of the starting and treated sepiolites were measured at -196 °C using a Micromeritic ASAP 2020 apparatus (static volumetric technique). The total specific surface areas (S<sub>BET</sub>) were determined through the BET equation (Brunauer et al., 1938). The specific mesopore pore volumes (V<sub>BJH</sub>) were calculated with the Barret–Joyner–Halenda method (Barrett et al., 1951). The average pore size (Wp) was determined approximating the pore geometry to a cylinder. The external specific surfaces areas (St<sub>ext</sub>), micropore areas (St<sub>micro</sub>) and micropore volumes (Vt<sub>micro</sub>) were estimated from t-plot method (Lippens and De Boer, 1965). In order to determine the influence of the temperature of degassing in the surface area values, adsorption–desorption isotherms were determined twice. Two aliquots (0.15 g) of each sample were outgassed for 16 h at 120 and 200 °C, respectively, under vacuum.

DRIFT spectra were collected on a Harrick HVC-DRP cell fitted to a Varian 3100 FT-IR spectrophotometer. The interferograms consisted of 200 scans, and the spectra were collected using a KBr spectrum as a background. About 30 mg of finely ground clay-based materials were placed in the sample holder.

The morphology of the starting sepiolites and the obtained materials were examined by scanning electron microscope (SEM) using a JEOL SM-6490 LV combined with X-ray energy dispersive spectroscopy (EDX). The samples for SEM observation were previously gold-sputtered (10 nm thick) in order to avoid charging of the surface.

# 3. Results and discussion

#### 3.1. X-Ray diffraction

Fig. 1 shows the X-ray diffraction patterns of the three starting sepiolites. The study of these profiles shows the mineralogical content of these samples. S1 was found to be pure or almost pure, whereas an almost negligible amount of calcite was found in S3. On the other hand, S2 has more mineralogical impurities than the other two samples (quartz, feldspar and opal CT). Variation in "crystallinity" (actually order/disorder) is a common feature in sepiolite samples of many deposits world-wide (Galán and Pozo, 2011). These variations can be studied through a detailed examination of the X-ray diffraction profiles. Fig. 1 shows the band component analysis of the X-ray diffraction profiles of the starting sepiolite samples. These patterns reveal significant differences in the characteristics of diffraction reflections. These may be interpreted in term of differences in "crystallinity" and/or chemical compositions. The differences in the d-spacing of the 110 reflection (Fig. 1a) have been attributed to modifications in the crystalline cell, originated by compositional variations



Fig. 2. XRD patterns of the starting sepiolites and obtained materials after acid treatment.



Fig. 3. Band component analysis of the XRD patterns of starting sepiolite S1 and materials obtained after 8 and 16 min with microwave-assisted HCl acid treatment.

caused by isomorphic substitution (Sanchez Del Rio et al., 2011). The higher iron content in sample S3 could explain the observed differences in the d-spacing produced by isomorphic substitution.

On the other hand, the band component analysis of the 110 reflection of the three studied sepiolites allows the detection of two components in this diffraction peak with differences related to both positions and the full width at half maximum (FWHM) of the components. Moreover, in the three starting sepiolites, the smaller reflection, centered at lower °20, has higher FWHM than the largest one. These results suggest the presence in each sample of, at least, two phases of sepiolite with different "crystallinity" and small differences concerning the chemical composition. The FWHM of the largest component of 110 peak of S1 (0.43°20) suggests that this is the most crystalline sample, whereas the FWHM of the 110 reflection of S2 (0.49°20) indicates that this sample contains the highest proportion of structural disorder. In this sense, S3 exhibits an intermediate FWHM value (0.45°20).

According to Pozo et al. (2014), the presence of well-defined reflections at 5.02, 3.00, 2.82, 2.67, 2.61, 2.58, 2.56, and 2.40 Å (Fig. 1b) similar to those observed in the XRD diffraction profiles of S1 and S3 samples, indicates that these samples are well ordered sepiolites (HCS). Moreover, the lowest FWHM of the peaks corresponding to S1 indicates that this is slightly more crystalline than S3. By contrast, the X-ray profile of S2 shows broader peaks, between 18 and 42°2, compared to those described above. In particular, the triplet at 2.61, 2.58 and 2.56 Å, which is very sensitive to the structural ordering, appears bad defined. This result suggests that this sample is relatively of lower "crystallinity" (LCS).

Fig. 2 shows the X-ray diffraction patterns of the starting sepiolites and the obtained products after the microwave-assisted treatment with HCl and HNO<sub>3</sub>. A first general observation is that during the first two minutes of treatment no significant changes were observed in the X-ray diffraction profiles. Moreover, the patterns reveal that the beginning of structural transformations occurs at shorter treatment times when HNO<sub>3</sub> is used. Indeed after 4 min employing this acid, the 110 reflection of S2 has significantly decreased compared to the intensity of that reflection in the untreated sample. However, if HCl is used, 8 min of treatment is necessary to identify the first evident changes in the diffraction profile of S2.

After 16 min of treatment with  $HNO_3$ , the 110 reflections of S1 and S2 have been almost eliminated, while the intensity of 110 reflection of S1 retains almost 50% of its initial intensity. By contrast, when HCl is used, the treatment time necessary to observe these structural modifications is markedly increased. The HCl acid is as effective as the  $HNO_3$  only in the case of S2, where the 110 reflection has been almost completely eliminated after 16 min of treatment.

The band component analysis of the X-ray diffraction profiles between 20 and  $40^{\circ}2\theta$  of the starting S1 and the obtained materials after 8 and 16 min of treatment with HCl (Fig. 3) reveal that reflections



Fig. 4. Mass loss with the different tested treatments.

Table 1	
Chemical analysis of starting sepiolites and obtained materials after acid treatmen	ıt.

	% SiO <sub>2</sub>	% MgO	% Al <sub>2</sub> O <sub>3</sub>	% K <sub>2</sub> O	% TiO <sub>2</sub>	% Fe <sub>2</sub> O <sub>3</sub>	% CaO	% MnO	% P <sub>2</sub> O <sub>5</sub>
S1	56.89	23.975	0.69	0.198	0.031	< 0.200	< 0.60	< 0.05	< 0.045
S1_HCL_2min	59.16	22.073	0.66	0.177	0.037	< 0.200	< 0.60	< 0.05	< 0.045
S1_HCL_4min	61.33	20.023	0.63	0.179	0.035	< 0.200	< 0.60	< 0.05	< 0.045
S1_HCL_8min	65.23	16.034	0.67	0.228	0.038	< 0.200	< 0.60	< 0.05	< 0.045
S1_HCL_16min	70.68	10.825	0.59	0.216	0.039	< 0.200	< 0.60	< 0.05	< 0.045
S1_HNO3_2min	60.64	21.039	0.68	0.181	0.038	< 0.200	< 0.60	< 0.05	< 0.045
S1_HNO3_4min	63.28	18.563	0.63	0.189	0.045	< 0.200	< 0.60	< 0.05	< 0.045
S1_HNO3_8min	67.44	14.174	0.66	0.217	0.036	< 0.200	< 0.60	< 0.05	< 0.045
S1_HNO3_16min	81.77	2.450	0.59	0.229	0.040	< 0.200	< 0.60	< 0.05	< 0.045
S2	63.18	18.820	1.67	0.438	0.078	0.275	< 0.60	< 0.05	< 0.045
S2_HCL_2min	67.81	14.934	1.72	0.454	0.085	0.30	< 0.60	< 0.05	< 0.045
S2_HCL_4min	67.76	14.783	1.74	0.461	0.084	0.255	< 0.60	< 0.05	< 0.045
S2_HCL_8min	72.97	10.148	1.66	0.454	0.088	< 0.200	< 0.60	< 0.05	< 0.045
S2_HCL_16min	84.3	1.365	1.84	0.544	0.093	< 0.200	< 0.60	< 0.05	< 0.045
S2_HNO3_2min	67.01	15.243	1.72	0.450	0.087	0.26	< 0.60	< 0.05	< 0.045
S2_HNO3_4min	69.73	13.265	1.67	0.447	0.082	0.248	< 0.60	< 0.05	< 0.045
S2_HNO3_8min	73.46	9.187	1.66	0.453	0.088	0.209	< 0.60	< 0.05	< 0.045
S2_HNO3_16min	84.53	1.274	1.86	0.592	0.094	< 0.200	< 0.60	< 0.05	< 0.045
S3	56.41	22.393	1.56	0.219	0.072	0.436	0.824	< 0.05	< 0.045
S3_HCL_2min	60.49	20.338	1.48	0.213	0.073	0.460	< 0.60	< 0.05	< 0.045
S3_HCL_4min	61.67	18.607	1.43	0.217	0.075	0.436	< 0.60	< 0.05	< 0.045
S3_HCL_8min	64.23	16.390	1.35	0.215	0.073	0.409	< 0.60	< 0.05	< 0.045
S3_HCL_16min	67.77	12.794	1.39	0.211	0.077	0.563	< 0.60	< 0.05	< 0.045
S3_HNO <sub>3</sub> _2min	60.28	20.078	1.50	0.213	0.074	0.456	< 0.60	< 0.05	< 0.045
S3_HNO <sub>3</sub> _4min	62.29	18.207	1.43	0.217	0.075	0.437	< 0.60	< 0.05	< 0.045
S3_HNO <sub>3</sub> _8min	63.82	17.284	1.40	0.213	0.074	0.436	< 0.60	< 0.05	< 0.045
S3_HNO <sub>3</sub> _16min	70.48	11.266	1.18	0.209	0.073	0.357	<0.60	< 0.05	< 0.045

located in this region suffer a progressive decrease in intensity and an increase in the FWHM. At the same time, a broad band appears centered at 25°20, whose intensity increases with the treatment time. This result suggests the occurrence of an amorphous phase or a phase of very low "crystallinity" whose proportion increases as the proportion of ordered sepiolite decreases.

It is interesting to note that the intensity of the induced effects depends not only on the acid used, but also on other factors such as crystallographic characteristics of the starting sepiolite. Apparently, the resistance to these treatments increases with the "crystallinity" of the sample. It seems that other factors such as the presence of other mineralogical phases do not have a clear influence on the effectiveness of these treatments.

# 3.2. Mass loss during treatment

In addition to structural changes, one of the most important consequences of this microwave-assisted acid treatment is the mass loss for the sepiolite samples during treatments. We take into account that the experimental method to calculate the mass loss can introduce some errors that are difficult to quantify. Nevertheless, calculating this mass loss gives important information about the effect of treatments on sepiolite. Fig. 4 shows the mass losses of the samples subjected to treatment with HCl and HNO<sub>3</sub>. In the case of treatment with HCl it has been observed that all the samples lost between 15 and 17% of its initial weight in the first 2 min of treatment. After this time the mass loss rate is slower and occurs at a constant rate approximately (1.5 wt.% min<sup>-1</sup>, in the case of S1). This result contrasts with that observed by XRD in which the major structural changes are observed after the first 8 min of treatment. This result suggests that the most important features of the crystalline structure still remain even if some of its elements are depleted in the first minutes of treatment.

On the other hand, the microwave-assisted treatment with HNO<sub>3</sub> originates slightly lower mass losses in the first two minutes of treatment compared with the HCl treatment. During this treatment time, sepiolite samples lost between 12 and 15% of its initial mass. From this treatment time, sepiolite samples lose mass steadily, being higher the

mass loss rate in the S1 and S2 samples (~1.7 wt.% min<sup>-1</sup>) and slightly lower in S3 (1.25 wt.% min<sup>-1</sup>).

# 3.3. Chemical analysis

The chemical compositions obtained by X-ray fluorescence of the natural sepiolites and materials resulting from the acid treatment are given in Table 1. It has not been possible to calculate the structural formula of sepiolite due to the presence of other mineralogical phases in the samples and the presence of at least two sepiolite phases with different crystalochemical characteristics in each sample as suggested by the XRD patterns.

A first observation of Table 1 reveals that, in general, microwaveassisted acid treatments cause the selective dissolution of  $Mg^{2+}$  ions of the octahedral sheet, in relation to the amount of Si remaining in the solid. Dissolution of  $Mg^{2+}$  ions is more pronounced in sample S2 in which this element disappears almost completely after 16 min of treatment with both acids. In this case, in addition to the lower "crystallinity" of this sample, we have to take into account the lower proportion of Mg in the starting sample due to the presence of other mineralogical phases such as feldspar and quartz, which do not include this element in their chemical composition. Moreover, these mineralogical phases contribute to the amount of Al in the global composition of the sample.

The drastic decrease in the Mg content is also observed during the treatment of S1 with HNO<sub>3</sub>. Nevertheless, the Mg loss is less marked if the treatment is done with HCl. Overall, data of Table 1 suggests that treatments with oxidizing acids, as HNO<sub>3</sub>, cause more intense dissolutions of Mg atoms of the octahedral sheet of sepiolite when compared with non-oxidizing acids, such as HCl treatments.

Table 1 shows that S3 has higher amounts of Fe and Al than S1 and S2. This fact can be related to the observed displacement of the 110 reflection to higher angles in the XRD profile of the starting sepiolites (Fig. 1a). Moreover, this sample has a small amount of Ca related to the presence of calcite. However, this element is not detected in the chemical analysis of the treated S3 samples, suggesting that calcite is quickly dissolved during the first 2 min of treatment. The S3 sample



Fig. 5. SEM micrographs of S1 (a), S2 (b) and S3 (c) samples.

shows a slower decrease of  $Mg^{2+}$  ions compared with S1 and S2 samples. Although, the small amount of calcite could decrease slightly the initial concentration of acid, the different leaching rates suggest that the presence of a higher proportion of  $Al^{3+}$  in the octahedral sheet influences the dissolution of  $Mg^{2+}$ .

## 3.4. Scanning electron microscopy

The SEM micrographs of the starting sepiolites (Fig. 5) show that sepiolite particles exhibit their characteristic fibrous morphology. The lengths of the individual fibers range between 1 and 15 µm. However,



Fig. 6. SEM micrographs of S1 HNO<sub>3</sub>-16 min (a) and S2 HNO<sub>3</sub>-16 min (b) samples.

there are significant differences in the proportion of each fiber population according to the individual fibers' length. Individual fibers longer than 6 µm are the predominant population in S1 (Fig. 5a), whereas in S3 fibers shorter than 2 µm are the main population (Fig. 5c). Sample S2 (Fig. 5b) shows a great homogeneity in the particle size. In this sample, the length of individual fibers is close to 4 µm. These fibers appear very rarely isolated and commonly forming aggregates. Suárez and García-Romero (2012) showed that sepiolite fibers commonly form flat tables which are made up of parallel or tangled fibers. In the case of S1 (Fig. 5a), fibers are associated by forming aggregates of block shapes. The sizes are higher than 20 µm and the porosity is minimal in the center and widens outwards, the outer fibers being partially attached to the external surface of the aggregate. These blocky aggregates are rarely visible in S2 and S3. In these samples the aggregates of tape-like shapes or flat tables are common as described by Suárez and García-Romero (2012). Therefore, we can conclude that the three starting sepiolites show large differences regarding size and morphology of their aggregates. In general, the scanning electron micrographs show that the largest aggregates are found in the S1 sample, the smallest aggregates in the S3 sample and the intermediate ones in the S2 sample.

The SEM images of the obtained samples after the microwaveassisted acid treatments show similar changes throughout the treatment (Fig. 6a and b). Initially, these treatments cause a slight disaggregation of the blocky aggregates, followed by a sharp decrease in the length of aggregates with tape-like shapes as well as in the length of the individual fibers. Finally, at longer treatment times the fibers end up losing their original fibrous morphology and acquire very irregular

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Fig. 7. Band component analysis of the DRIFT spectra of the starting sepiolites. a) 3850-2700 cm<sup>-1</sup> region. b) 1800-600 cm<sup>-1</sup> region.

shapes, the smallest ( $<0.2 \ \mu m$ ) particles being almost globular. These particles with irregular morphologies usually appear associated in aggregates. When sepiolite shows a greater resistance to the tested treatments, as S1 does, it can be seen that even after 16 min of treatment fibrous particles still coexist with those particles of irregular morphologies (Fig. 6a). In cases in which the sepiolite shows higher reactivity (e.g. sample S2) it is possible to check the total disappearance of fibrous particles after 16 min of treatment (Fig. 6b).

# 3.5. DRIFT spectroscopy

The hydroxyl-stretching region of the DRIFT spectra of the three starting sepiolite samples are shown in Fig. 7a. According to Frost et al. (2001), in this region sepiolite shows two bands at 3689, and 3633 cm<sup>-1</sup> which are associated with the stretching vibration of the hydroxyls coordinated with magnesium; a band at 3564 cm<sup>-1</sup> related with the stretching modes of molecular water coordinated with magnesium, and two bands at 3359 and 3245 cm<sup>-1</sup> that have been attributed to zeolitic and coordinated water (Frost et al., 1998). Nevertheless, in order to adjust properly the spectral region where the latter two bands are present it is necessary to use four bands at 3463, 3355,

3224 and 3172 cm<sup>-1</sup> in the band component analysis. This result suggests the existence of, at least, four different environments in which the structure of sepiolite can adsorb water molecules.

Previous studies have shown that there are several types of water present in sepiolite (Van Der Marel and Beutelspacher, 1976). The best spectroscopic method for studying water is to examine the H– O–H bending mode centered at 1630 cm<sup>-1</sup>. In this region of spectra, this band does not overlap with the hydroxyl stretching frequencies of sepiolite. In Fig. 7b, two major bands are observed at 1666 and 1627 cm<sup>-1</sup> for the three starting sepiolites. Following Farmer (1974), these bands can be attributed to the zeolitic and adsorbed water respectively. A small shoulder centered at 1704 cm<sup>-1</sup> can be assigned to water molecules very strongly bonded (Frost et al., 2001). In the DRIFT spectra of S3 it is possible to identify a band at 1469 cm<sup>-1</sup> attributed to the (CO<sub>3</sub>)<sup>2–</sup> antisymmetric and symmetric stretching modes which confirms the presence of carbonate impurity as shown by XRD.

According to Frost et al. (2001), bands between 1225 and 1000 cm<sup>-1</sup> are assigned to Si–O stretching modes, whereas those between 1000 and 700 cm<sup>-1</sup> are attributed to M–OH deformation, and bands between 700 and 600 cm<sup>-1</sup> can be related to the M–OH translation. When the DRIFT



Fig. 8. Band component analysis of the DRIFT spectra of the starting S2 and obtained materials after acid treatment with HNO<sub>3</sub>. a) 3850–2700 cm<sup>-1</sup> region. b) 1800–600 cm<sup>-1</sup> region.

spectra of the three sepiolite samples are compared, some differences may be observed. These can be explained in terms of differences in "crystallinity" (Pozo et al., 2014) and differences in chemical compositions. High "crystallinity" sepiolites (HCS), such as S1 and S3, show well defined doublet at 1212 and 1194 cm<sup>-1</sup>, whereas in low "crystallinity" sepiolites (LCS), such as sample S2, these bands appear notably broadened. In the last case a third band centered at 1243 cm<sup>-1</sup> is necessary to fit the band component analysis in this region of the spectra. On the other hand, the shifting to lower wavenumbers of the M–OH deformation band at 976 cm<sup>-1</sup> shown in S3 could be explained by a higher proportion of isomorphous substitution of Mg for Al in the octahedral sheet.

Fig. 8a shows the band component analysis of the OH stretching region of S2 and the obtained materials after the microwave-assisted acid treatment with HNO<sub>3</sub>. These patterns show the appearance of a small band a 3733 cm<sup>-1</sup> in the first 2 min of treatment. This band is commonly observed in the acid treated minerals and it is related to the Si–OH groups (Komadel and Madejová, 2006). Moreover, these spectra reveal a slight decrease in the intensity of the OH stretching bands at 3689, 3633 and 3564 cm<sup>-1</sup>. The band at 3689 cm<sup>-1</sup> disappears completely after 16 min of treatment, whereas the bands at 3633 and 3564 cm<sup>-1</sup> are progressively broadened and shifted to higher and lower wavenumbers, respectively. These results suggest the complete loss of the OH groups coordinated with Mg along the entire treatment of S2. A similar behavior can be observed in the DRIFT spectra of the other samples obtained with both acid treatments (Fig. 9). However, the complete loss of the OH stretching bands is not observed in all cases. This indicates that sepiolite samples exhibit different reactivities to the tested treatments.

Fig. 8b shows the corresponding band component analysis of 1800– 600 cm<sup>-1</sup> region of the DRIFT spectra of samples shown in Fig. 8a. The most obvious changes in this region of the spectrum are related to the bands of the Si–O stretching modes. These bands are progressively replaced with wider bands causing a significant change in the profile of the DRIFT spectrum. After 16 min of treatment this region of the spectrum is composed of three distinct zones: zone 1 (between 1325 and 996 cm<sup>-1</sup>), zone 2 (between 996 and 850 cm<sup>-1</sup>), and zone 3 (between 850 and 725 cm<sup>-1</sup>). The first zone could be related with the Si–O–Si stretching band of low "crystallinity" phases originated in the treatment. In this sense, Valentín et al. (2007) related the change in shape and frequency of the bands present in this zone with the formation of amorphous silica. Nevertheless, they found these modifications after



Fig. 9. DRIFT spectra of starting sepiolites and obtained materials outgassed at 200 °C.

45 min of treatment. In our case these changes occur notably less at treatment time, between 8 and 16 min. In a similar way, the absence of the M–OH group, suggests that bands of zone 2 can be assigned to the vibrational modes of the free silica (Madejová et al., 1998).

This result suggests that the water loss from sepiolite channels during the drastic structural transformation was caused by the acid treatments.

#### 3.6. Nitrogen adsorption

Fig. 8b also reveals interesting information on the type of water which remains in the structure of sepiolite after acid treatments. In this case it can be seen that the characteristic band of the zeolitic water (1666 cm<sup>-1</sup>) decreases in intensity along the processing while band related with adsorbed water (1627 cm<sup>-1</sup>) remains unchanged.

The nitrogen adsorption–desorption isotherms for the three starting sepiolites and obtained products are shown in Fig. 10. These isotherms correspond to type II of the International Union of Pure and Applied Chemistry (IUPAC) classification (Sing et al., 1985). All of the studied samples present very small hysteresis loops corresponding to Type



Fig. 10. Nitrogen adsorption-desorption isotherms of starting sepiolites and obtained materials outgassed at 200 °C.

H4, which suggests the presence of narrow slit-shaped pores (Sing et al., 1985). Suárez and García-Romero (2012) showed that there are many factors that influence surface properties, including mineralogical impurities, differences in "crystallinity" and arrangement of the fibers. They described two types of porosity (microporosity (structural and interfiber) and mesoporosity) related to the specific surface area.

The main results of the textural analysis, of the starting sepiolites and the obtained materials, are shown in Table 2. First it is necessary to take into account that in order to obtain surface area values close to real values, samples must be properly outgassed. For this reason, to find the appropriate conditions for the analysis of the samples, they were kept for 16 h at two different temperatures (120 and 200 °C). Table 2 shows that surface area values are notably influenced by the temperature used to outgas the sample. When analyzes were performed after heating at 200 °C, the three starting sepiolite exhibit similar external surface area ( $S_{ext}$ ), similar and very small microporous area ( $S_{micro}$ ), and, therefore, similar BET surface area ( $S_{BET}$ ). In addition, values of  $S_{BET}$  are notably smaller than the reported in the literature (Pozo et al., 2014). On the contrary, when samples were outgassed at 120 °C the estimated  $S_{micro}$  and  $S_{BET}$  values of natural sepiolites are notably higher compared to those obtained after outgassing at 200 °C and different from them. These results suggest that the surface area from samples outgassed at 200 °C is strongly influenced by some textural or structural modification, which affects strongly the microporous surface area (Table 2).

Table 2	Та	bl	e	2
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Specific surface areas, pore volumes and pore diameters, obtained after outgassing at 200 °C or 120 °C of starting sepiolites and obtained materials after acid treatment.

Sample	$S_{BET} (m^2 g^{-1})$	$\frac{\text{St}_{\text{ext}}}{(\text{m}^2\text{g}^{-1})}$	St $_{micro}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{BJH}$ (cm <sup>3</sup> g <sup>-1</sup> )	Vt micro (cm <sup>3</sup> g <sup>-1</sup> )	Wp (nm)	$S_{BET} (m^2 g^{-1})$	St $_{ext}$ (m <sup>2</sup> g <sup>-1</sup> )	St $_{micro}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{BJH}$ (cm <sup>3</sup> g <sup>-1</sup> )	Vt micro (cm <sup>3</sup> g <sup>-1</sup> )	Wp (nm)
	200 °C						120 °C					
S-1	117	102	15	0.37	0.008	12.9	288	117	171	0.37	0.077	12.2
S-1 2 min HCl	155	118	37	0.39	0.019	10.2	294	144	150	0.44	0.068	11.8
S-1 4 min HCl	216	139	77	0.42	0.040	7.8	277	170	107	0.49	0.048	12.1
S-1 8 min HCl	361	188	173	0.52	0.089	5.9	334	199	135	0.54	0.061	11.0
S-1 16 min HCl	459	229	230	0.63	0.120	5.5	407	352	55	0.66	0.018	8.9
S-1 2 min HNO3	175	132	43	0.41	0.023	9.5	327	161	166	0.45	0.076	10.8
S-1 4 min HNO3	244	150	94	0.44	0.050	7.2	358	173	185	0.50	0.083	10.8
S-1 8 min HNO3	378	191	187	0.56	0.100	5.9	406	222	184	0.56	0.083	9.8
S-1 16 min HNO3	519	437	82	0.73	0.042	5.6	437	348	89	0.63	0.037	8.2
S-2	128	111	17	0.38	0.008	11.9	252	128	124	0.38	0.054	11.7
S-2 2 min HCl	212	149	63	0.44	0.033	8.4	285	172	113	0.47	0.050	11.4
S-2 4 min HCl	270	160	110	0.45	0.051	7.1	272	184	88	0.48	0.038	10.7
S-2 8 min HCl	323	188	135	0.49	0.072	6.1	309	222	87	0.48	0.039	9.0
S-2 16 min HCl	385	348	37	0.59	0.018	6.1	341	325	16	0.54	0.003	7.5
S-2 2 min HNO3	206	144	62	0.43	0.032	8.3	248	161	87	0.43	0.047	10.2
S-2 4 min HNO3	296	158	138	0.46	0.059	6.9	261	171	90	0.37	0.044	8.9
S-2 8 min HNO3	366	220	146	0.56	0.078	6.2	275	110	165	0.37	0.067	15.1
S-2 16 min HNO <sub>3</sub>	433	317	116	0.66	0.063	6.1	293	279	14	0.46	0.004	7.5
S-3	133	111	22	0.53	0.012	15.8	320	127	193	0.56	0.087	16.7
S-3 2 min HCl	282	156	126	0.71	0.057	10.1	289	159	130	0.65	0.059	15.9
S-3 4 min HCl	370	181	189	0.83	0.083	8.9	315	165	150	0.69	0.068	16.2
S-3 8 min HCl	400	182	218	0.89	0.099	8.1	357	197	160	0.77	0.073	14.2
S-3 16 min HCl	410	197	213	0.89	0.096	7.9	320	203	117	0.67	0.052	12.9
S-3 2 min HNO <sub>3</sub>	154	133	21	0.52	0.010	13.4	328	170	158	0.67	0.072	14.8
S-3 4 min HNO <sub>3</sub>	323	187	136	0.81	0.061	10.0	280	174	106	0.69	0.047	15.8
S-3 8 min HNO3	371	174	197	0.84	0.088	8.0	317	176	141	0.71	0.063	14.2
S-3 16 min $HNO_3$	438	197	241	0.82	0.109	7.5	396	205	191	0.75	0.087	13.3

In general, an increase of BET surface area is observed from the first minutes of treatment that is accompanied by an increase in the pore volume and a decrease in the pore diameter (Table 2, Fig. 11). This increase in surface area has been classically related to the appearance of an amorphous silica phase due to the partial dissolution of the octahedral sheet of sepiolite with the acid treatment (Vicente Rodríguez et al., 1994). Contrary to those observed in natural samples, higher values of surface area of the treated sepiolites are usually observed in samples outgassed at 200 °C. In most cases, there is a clear correlation between the proportion of amorphous silica in the sample and the difference in the surface area obtained with both outgassing temperatures. Some samples show variations of 140  $m^2/g$  with these two different procedures. These results suggest the existence of water molecules strongly retained on the surfaces of formed amorphous silica which are evacuated at temperatures close to 200 °C. Thus, heating at lower temperatures does not outgas completely the sample resulting in masked surface values. It should be noted that the starting sepiolites and the obtained materials have notably crystallochemical differences and, therefore, they have water molecules sorbed in very different environments.

Taking into account these previous considerations, the nitrogen adsorption data reveal an increase in the BET surface area and pore volume parallel to the increase in the proportion of silica with the treatment. These increases in surface area are significantly higher when treatments are performed with HNO<sub>3</sub> and in the HCS sepiolites. Moreover, in all cases it was found that the assistance of microwaves during the acid treatment allows obtaining, after 16 min of treatment, materials with surface areas equivalent to those obtained after 48 h with conventional heating methods (Vicente Rodríguez et al., 1994).

# 4. Conclusions

The microwave-assisted acid treatment has proved to be an effective method to activate sepiolite. Using this type of treatment it is possible to obtain, in just a few minutes, materials whose BET surface areas are similar to those materials activated by traditional methods in two days, despite employing acid solutions of very low concentrations. These facts make this method an optimized treatment very interesting for industrial purposes.

The results have revealed that microwave-assisted acid treatment causes a progressive amorphization of the starting sepiolite giving rise to the formation of sepiolite with partially disrupted structures and an increasing amount of amorphous silica, which is accompanied by a huge mass loss, due to the  $Mg^{+2}$  depletion of the octahedral sheet. Nevertheless, the chemical analysis and the XRD data suggest that the structure remains, at least partially, even after 43% of  $Mg^{2+}$  is lost. Consequently, the characteristic fibrous morphology of natural sepiolite remains in acid-activated materials with partially dissolved structures. However, when  $Mg^{2+}$  is completely released the fibrous shape disappears, generating particles of amorphous silica with globular-like irregular morphologies.

The use of sepiolites with differences in structural order and chemical compositions, and the use of different acids have allowed determining the most important factors that control the intensity of the induced changes with the acid activation. The treatment with HNO<sub>3</sub> is much more effective than HCl, at least, in the tested times.

The microwave-acid treatment effectiveness depends also on the starting sepiolite's own characteristics. The lower crystalline sepiolite tends to lose easily its structure completely with these treatments, but the presence of  $AI^{3+}$  in octahedral sheets seems to have a negative influence on the rate of dissolution. Factors such as the presence of mineralogical impurities do not affect the effectiveness of this novel acid activation.

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Fig. 11. Evolution of the BET specific surface area (SBET) vs. time of treatment after outgassing at 120 or 200 °C.

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