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Additional Information

**“Characterization of selectively etched halloysite nanotubes by acid treatment”**

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## Abstract

Halloysite nanotubes (HNTs) are a type of naturally occurring inorganic nanotubes that are characterized by a different composition between their external and internal walls. The internal walls are mainly composed of alumina whilst external walls are composed of silica. This particular structure offers a dual surface chemistry that allows different selective surface treatments which can be focused on increasing the lumen, increasing porosity, etc. In this work, HNTs were chemically treated with different acids (sulphuric, acetic and acrylic acid), for 72 h at a constant temperature of 50 °C. As per the obtained results, the treatment with sulphuric acid is highly aggressive and the particular shape of HNTs is almost lost, with a remarkable increase in porosity. The BET surface area increases from 52.9 (untreated HNTs) up to 132.4 m<sup>2</sup> g<sup>-1</sup> with sulphuric acid treatment, thus showing an interesting potential in the field of catalysis. On the other hand, the treatment with acetic acid led to milder effects with a noticeable increase in the lumen diameter that changed from 13.8 nm (untreated HNTs) up to 18.4 nm which the subsequent increase in the loading capacity by 77.8%. The aluminium content was measured by X-ray fluorescence (XRF) and laser induced breakdown spectroscopy (LIBS). The final results using two systems, suggest a good correlation between the acid strength and the aluminium reduction. Consequently, is possible to conclude that new applications for HNTs can be derived from selective etching with acids. Sulphuric acid widens the potential of HNTs in the field of catalysis while weak acids such as acetic and acrylic acids give a controlled and homogeneous lumen increase with the corresponding increase in the loading capacity.

**Keywords:** Halloysite nanotubes; lumen enlargement; acid treatment; catalysis; LIBS.

## 1. Introduction

One of the main features of nanomaterials is their high surface to volume ratio which gives an exponential increase in the reactivity of the molecules thus leading to a remarkable change in their electronic, optical, chemical or mechanical properties with regard to their bulk counterpart materials. For this reason, nanomaterials offer a great potential in a wide range of research areas such as biomedicine, cosmetics, food and food packaging, coatings, electronics, catalysis or materials sciences [1]. A wide variety of metal oxides, nanoclays, carbon nanomaterials, organometallic nanocomposites (MOFs) have been successfully introduced in new materials [2], with the particular feature that nanoparticles offer a strong different behavior than their counterpart micro/macro particles. Nanoclays have been widely studied as support for different catalysts [3]. In particular, the petroleum industry is leading the introduction of nanoparticles as supports for catalysts in several reactions. It has been reported the potential of activated carbon and carbon nanotubes (CNTs) as support for ethanol oxidation [4], aluminosilicates, cordierites [5], zeolites [6], other feldspars, kaolinite derivate such sespiolites [7], HNTs, etc., which allow the conversion of crude oil in a wide range of products. Nanomaterials are continuously acquiring new features in the catalysis industry. Abbasov *et al.* [8] reported the positive effects of a previous acid treatment on HNTs with HCl to improve the efficiency as support for NiO and CoO for fuel production from heavy crude oil. Zhang *et al.* [9] used a silane treatment with aminopropyltriethoxysilane as a previous treatment to increase Pd adsorption on HNTs as catalytic system for the conversion of styrene to ethylbenzene. In a parallel way, CNTs are also being investigated as support for different catalysts [10]. Nevertheless, the use of CNTs is restricted in the medicine field due to their potential health risks. On the other hand, their high cost is a key disadvantage for a wide use in the field of composites.

Other important application of nanoparticles is hydrogen storage on micro/nanoporous materials [11]. Many of the abovementioned materials are intrinsically porous or can be modified to increase the overall porosity and surface area. Another feature of porous nanoparticles is related to their potential use as container for controlled drug release [12]. Despite it is true that a wide variety of encapsulated structures for controlled delivery are currently used, aluminosilicates own

a privileged position due to their low cost and health safety. Aluminosilicates are currently being used for controlled delivery of antimicrobials in the cosmetic industry [13], non-foaming oxygen nanocontainer [14], support of compatibilizer agents in immiscible polymer blends [15], flame retardant containers [16, 17], heavy metal nanoadsorbers [18], with a remarkable effect on the prolonged effect with time [19]. In addition, aluminosilicates can be loaded with active additives such as thermal stabilizers, antioxidants, UV light stabilizers, etc. to protect polymers for prolonged exposure to environment. The use of aluminosilicates HNTs has been widely reported in polymer formulations to improve mechanical properties [20, 21]; also, their use in the food-contact products is increasing as HNTs can provide controlled delivery of preservatives, antibacterials and others [22].

HNTs have been also used in pharmacology, prosthesis [23], bone repairing and therapy against cancer [24]. HNTs are characterized by extremely high biocompatibility [25]. They are good drug carriers for controlled drug release [26, 27]. Qi *et al.* [28] manufactured nanofiber mats with poly(lactide-*co*-glycolide) with HNTs previously loaded with tetracycline hydrochloride antibiotic. Other aluminosilicates nanotubes, i.e. imogolite nanotubes, were successfully used as scaffolds for cell growth [29].

The particular aluminosilicate structure of HNTs with an internal alumina layer and an external silicate layer allows a wide variety of chemical modifications such as acid [30-32], alkali [33] and other [34] to selectively change porosity, lumen size, surface activity, etc. Acid treatments promote the removal of Al<sub>2</sub>O<sub>3</sub> while an alkaline treatment preferably attacks the silica layer. Both the acid and the alkali treatments lead to electrically charged structures which play a key role in substance absorption. Different research works have been done in the last years, focused on HNTs modification. Abdullayev *et al.* [35] used sulphuric acid at different concentrations and treatment-times with the main aim of increasing the average diameter of the HNTs lumen. They reported an increase in the load capacity by 2 to 3 times higher regarding the initial capacity. Wang *et al.* [36] studied the effect of several concentration of hydrochloric acid (HCl) on the morphology, the crystalline structure and the porous texture of HNTs. They concluded that very slight changes in the crystalline structure and the hollow shape were obtained

with this treatment. Nevertheless, to our knowledge, an in depth comparative study of the effects of different acids (including sulphuric acid which is the most used for this treatments) on chemical and morphological changes of HNTs has not been carried out.

The present work explores the effect of the strength of different acids (sulphuric, acrylic and acetic acids) on the morphology of chemically modified HNTs to define their possibilities in the field of catalysis and/or container for controlled delivery. The novelty of the present work is focused on the use of weak acids, i.e. acetic and acrylic acids, to treat HNTs and study their effect on the chemical changes and morphology, compared to the effects of a widely used acid for this type of treatments, sulphuric acid. The work covers the use of different techniques (transmission electron microscopy (TEM), X-ray fluorescence (XRF), X-ray diffraction spectroscopy (XRD), laser induced breakdown spectroscopy (LIBS), thermogravimetric analysis (TGA), specific surface area (BET) to give new insights on the chemical changes produced by acid treatment on HNTs.

## **2. Materials and methods**

### **2.1. Materials**

Halloysite nanotubes were supplied by Sigma Aldrich (Madrid, Spain). Sulphuric acid (95%  $\text{H}_2\text{SO}_4$ ) and acetic acid (99.7%  $\text{CH}_3\text{COOH}$ ) were supplied by PanReac AppliChem (Barcelona, Spain) and acrylic acid (99%  $\text{CH}_2=\text{CHCOOH}$ ) was obtained from Sigma Aldrich (Madrid, Spain). All reagents were used without any other purification.

### **2.2. Selective etching of HNT by acid treatment**

An acid treatment was carried out on HNTs which allows a selective etching of the alumina located in the interior parts of HNTs with a similar procedure as that described by Abdullayev *et al.* [35]. In summary, HNTs were previously dried overnight at 100 °C. Then, 5 g of HNTs were poured into 500 ml of the corresponding acid solutions with a constant concentration of 1 mol  $\text{L}^{-1}$ . The obtained suspension was maintained with magnetic stirring for 72 h on a hot plate at 50 °C. After this stage, chemically modified HNTs were collected by

centrifugation and washed with distilled water until the obtained pH was in the 6-7 range. Finally, HNTs were dried at 50 °C for 24 h prior to further characterizations.

## **2.3. Characterization techniques**

### ***2.3.1. Transmission electron microscopy (TEM)***

The morphology and size distribution of raw HNTs and the etched-HNTs were studied by transmission electron microscopy (TEM) in a Philips mod. CM10 (Eindhoven, the Netherlands) using an acceleration voltage of 100 kV. Prior to TEM observation, a small amount of the corresponding HNTs samples was dispersed in acetone immersed in an ultrasound bath; subsequently, a drop of this dispersion was poured onto a carbon grid and subjected to solvent evaporation at room temperature. The lumen size of HNTs was obtained from the collected TEM images and a minimum of 50 measurements were done to obtain the size distribution.

### ***2.3.2. X-ray fluorescence spectroscopy (XRF)***

The chemical composition of HNTs before and after the corresponding acid treatments was obtained by X-ray fluorescence spectroscopy in a sequential X-ray spectrometer PHILIPS MAGIX PRO PW2400 (Panalytical B.V., The Netherlands) equipped with a rhodium tube and a beryllium window. Results of the chemical compositions were analyzed by using the SuperQ analytical software. Each treated-sample was subjected to three different analyses and the average values were calculated.

### ***2.3.3. Laser induced breakdown spectroscopy (LIBS)***

LIBS analysis of raw and chemically etched HNTs was performed by a  $\mu$ -LIBS system based on a MODI' LIBS equipment (Mobile Dual-Pulse Instrument) [37]. The system is equipped with a double-pulse Nd:YAG laser, emitting at 1064 nm with pulse energy up to 60 mJ (20 ns FWHM pulse width). Laser radiation was focused through an optical microscope model Axio Scope A1 (Zeiss, Germany) on the sample to analyse. The microscope is equipped with a 10x objective having a focal distance of 10 mm. For LIBS analysis, the sample was placed on a

motorized stage which develops a 2D scanning of the sample surface. The optical signal from the laser-induced plasmas was collected by an optical fibre, placed at an angle of about 45 degrees and at a distance of 10 mm from the laser spot, and then sent to a broadband spectrometer model AvaSpec-2048-2 from Avantes (Eerbeek, The Netherlands) covering the spectral range comprised between 180 and 900 nm. The synchronization between the laser firing, data acquisition and x-y movement of the motorized stage was obtained using Labview® software. Data processing was performed by the spectroscopic software of the MODI' instrument (LIBS++®, v 5.0, ALS LAB). In this study, the Nd:YAG laser was operated at a pulse energy of 40 mJ. Double pulse LIBS analysis was performed in collinear mode, with 1  $\mu$ s delay between both laser pulses. LIBS spectra were acquired 1.3  $\mu$ s after the second laser pulse, with 2.5 ms acquisition time.

The HNTs samples were pressed into pellets for LIBS analysis, in order to avoid the powdered material to be ejected out due to the laser-induced shock wave. Circular pellets of about 25 mm diameter and 3 mm thickness were obtained by pressing the powder with an automatic mounting press machine Buehler SimpliMet 1000 (Illinois, USA) at a pressure of 200 bar during 10 min, after a previous mixing with KBr as the binder component. For quantitative LIBS analysis using standard addition calibration, a series of standards were prepared by mixing a fixed amount of halloysite (1.5 g) with increasing amounts of alumina. The standards were finally adjusted to the same final weight (2.5 g) by addition of KBr binder.

The analysis of the samples was carried out by programming a matrix of 10 x 3 laser shots separated 200  $\mu$ m in the central part. The resulting LIBS spectra were collected, averaged and processed by the spectroscopic LIBS++ software. All the data shown correspond to the mean value of three replicate measurements.

#### ***2.3.4. Porous texture***

The porous texture characterization of untreated and selectively etched HNTs was carried out by nitrogen adsorption-desorption at 77 K with a Autosorb-6 volumetric equipment from Quantachrome Instruments (Odelzhausen, Germany). All the samples were outgassed at 250 °C



under vacuum for 8 h prior to adsorption experiments. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) [38] procedure. The pore volume was determined by the nitrogen adsorption volume at a relative pressure ( $P/P_0$ ) of around 0.96. The mesopore size distribution was obtained by the Barret-Joyner-Halenda (BJH) method from the data collected from the corresponding nitrogen adsorption isotherm [39]. The measurements of each sample were repeated three times for each sample to ensure their accuracy.

### 2.3.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of all HNTs samples was carried out using the experimental methodology previously proposed for Zhang *et al.* [40] to characterize raw HNTs and HNTs treated with sulphuric acid. The analysis was conducted in duplicate for each sample in a TGA/SDTA 851e thermobalance from Mettler-Toledo (Schwerzenbach, Switzerland) under nitrogen atmosphere at a constant flow rate of 50 mL min<sup>-1</sup>. Samples with an average weight of 3-5 mg were placed into standard alumina crucibles (70  $\mu$ L) subjected to a dynamic heating program from 25 °C to 700 °C at a constant heating rate of 10 °C min<sup>-1</sup>.

### 2.3.6. X-ray diffraction spectroscopy (XRD)

The crystal structure of raw HNTs and chemically etched HNTs was determined by X-ray diffraction on a Bruker CCD-Appex apparatus equipped with a X-ray generator (Ni filtered Cu-K $\alpha$  radiation) operated at 40 kV and 40 mA. Samples in powder form were scanned from 5° to 90° (2 $\theta$ ) at a step of 2° min<sup>-1</sup>, following the experimental methodology proposed by Bordeepong *et al.* [41].

## 3. Results and discussion

### 3.1. Effect of selective acid treatment on the morphology of HNTs

Fig. 1 shows the TEM images and the size distribution of the lumen diameter of raw HNTs and the selectively etched HNTs by acid treatment. The morphology of the unmodified

HNTs can be observed in **Fig. 1a** with the typical tube shape. Unmodified HNTs possess an average lumen diameter of  $13.8 \pm 1.4$  nm with an external diameter ranging from 30 to 70 nm (average external diameter of 50 nm) [42]. With regard to their length, it is comprised between 1 and 3  $\mu$ m as measured and in total agreement with the information provided by the supplier. After the selective etching by acid treatment, remarkable changes can be observed. With regard to the acid treatments with acetic and acrylic acids (**Fig. 1c** and **Fig. 1d** respectively) an interesting increase in the average lumen diameter is obtained. In particular, the lumen diameter increases up to  $18.4 \pm 2.9$  and  $17.1 \pm 2.1$  nm with the acetic and acrylic acid treatments, which represents a percentage increase of 33.3% and 23.9% respectively compared to untreated HNTs. This increase also leads to a remarkable increase in the lumen volume, which increases by 77.8% for the acetic acid-etched HNTs and up to 53.5% for HNTs chemically etched with acrylic acid with regard to the initial lumen volume of untreated HNTs. This involves a noticeable increase in the potential of HNTs as carriers for different loads. It is worthy to note that both acid treatments with acetic and acrylic acid do not change the morphology in a great extent without any evidence of pore formation and breakage. Nevertheless, the morphology of HNTs chemically etched by sulphuric acid (**Fig. 1b**) is noticeably different to previous acid treatments. The lumen diameter (average size) is increased up to values of about  $31.6 \pm 6.7$  nm but as the TEM image suggests, the treatment with sulphuric acid is so aggressive and, as it can be seen, a highly porous structure, partially decomposed morphology can be detected. While the average lumen size for HNTs treated with acetic and acrylic acids follows a relatively narrow distribution, in the case of HNTs treated with sulphuric acid, the average diameter offers a wider distribution which gives evidences of partial decomposition due to aggressive etching. This is due to the fact that sulphuric acid is able to react with both the internal and external HNTs layers with a clear peeling effect on the external layer which contributes to the complete destruction of the internal hollow tube morphology as Zhang *et al.* concluded [40].

**Fig. 1**

### 3.2. Effect of selective acid treatment on the chemical composition of HNTs

The effects of the etching by acid treatment on the chemical composition of HNTs were studied by X-ray fluorescence spectroscopy. In a typical HNTs the silicon atom is combined with four adjacent oxygen atoms whilst each aluminium atom is coordinated with two hydroxyl groups and an additional oxygen atom as indicated by Yah *et al.* [32]. **Table 1** summarizes the compositions for neat HNTs and acid-treated HNTS. As it can be seen, presence of both silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) is in total agreement with the chemical structure of a typical aluminosilicate. In fact, both silica and alumina represent more than 98% of the total composition while the remaining ( $\text{P}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_3$ ,  $\text{CaO}$ ,  $\text{TiO}_2$  and  $\text{MgO}$ ) only represents a very small proportion (less than 2%). As it can be seen in **Table 1**, the alumina content decreases with both weak acid treatments, while this decrease is remarkable for the strong sulphuric acid treatment. This decrease in the alumina content could be related to the lixiviation of  $\text{Al}^{3+}$  cations from the octahedral layer due to the hydrolysis in acid conditions as reported by Panda *et al.* [43]. **Table 2** shows the atomic percentage of the main chemical elements (oxygen, silicon and aluminium) present in HNTs obtained by XRF. As it can be seen, the Si/Al ratio in unmodified HNTs is close to 1.1. Nevertheless, after the acid treatment with sulphuric acid, the Si/Al ratio increases up to values around 1.5 due to the selective etching of the interior alumina layers. Sulphuric acid preferentially dissolves the interior  $\text{AlO}_6$  layers leading to the collapse of the external tetrahedral  $\text{SiO}_6$  layers thus leading to a highly porous morphology mainly consisting on amorphous silicon as reported by Zhang *et al.* [40]. Regarding the Si/Al ratio for HNTs treated with weak acids such as acetic and acrylic, it remains with typical values of untreated HNTs with values close to 1.1. This is also in accordance with the mild effects of these acid treatments compared to the strong effects that sulphuric acid provides. As it can be seen in **Table 2**, the overall amount of aluminium decreases with the acid treatments. This decrease is much higher with the etching action of strong acids such as sulphuric.

**Table 1.** Chemical composition of untreated and chemically etched HNTs with different acids as obtained by XRF analysis.

Compound	Sample			
	HNTs	ACR-HNTs	ACE-HNTs	SUL-HNTs
SiO <sub>2</sub>	53.75 ± 0.64	53.96 ± 0.09	54.45 ± 0.27	61.64 ± 0.18
Al <sub>2</sub> O <sub>3</sub>	44.57 ± 0.67	44.26 ± 0.09	43.92 ± 0.07	36.71 ± 0.17
P <sub>2</sub> O <sub>5</sub>	0.64 ± 0.04	0.77 ± 0.03	0.65 ± 0.02	0.47 ± 0.02
SO <sub>3</sub>	0.29 ± 0.03	0.20 ± 0.05	0.21 ± 0.03	0.24 ± 0.02
CaO	0.12 ± 0.02	0.18 ± 0.03	0.15 ± 0.02	0.25 ± 0.01
TiO <sub>2</sub>	0.02 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.04 ± 0.00
Fe <sub>2</sub> O <sub>3</sub>	0.38 ± 0.02	0.38 ± 0.01	0.35 ± 0.05	0.31 ± 0.03
MgO	0.07 ± 0.06	0.06 ± 0.10	0.05 ± 0.09	0.20 ± 0.01
Sum	99.84	99.85	99.86	99.86
LOI	0.16	0.15	0.14	0.14

**Table 2.** The atomic equivalent of the major elements in untreated and chemically etched HNTs with different acids measured by XRF analysis.

Sample	Element content (atm%)			
	O	Si	Al	Si/Al
HNTs	50.34 ± 0.03	25.13 ± 0.30	23.59 ± 0.35	1.07 ± 0.03
ACR-HNTs	50.36 ± 0.02	25.22 ± 0.04	23.42 ± 0.05	1.08 ± 0.01
ACE-HNTs	50.38 ± 0.02	25.45 ± 0.13	23.24 ± 0.04	1.09 ± 0.01
SUL-HNTs	50.80 ± 0.07	28.81 ± 0.08	19.43 ± 0.10	1.49 ± 0.01

In addition to XRF, a new approach to the characterization of the effects of different acid etching on chemical composition of HNTs has been studied using LIBS. This technique is based on focusing a laser beam on a small area of the sample to analyse, resulting in the generation of a highly energetic plasma in which the sample is atomized, ionized and excited. Spectral resolution of plasma emission provides qualitative and quantitative information on the sample content. A

preliminary qualitative analysis was performed in order to identify the elements presents in untreated HNTs. **Fig. 2** shows a LIBS spectrum corresponding to untreated HNTs. As it can be seen, most of the emission lines appearing in the LIBS spectrum of untreated HNTs correspond to the more abundant elements: aluminium, silicon and oxygen. Moreover, LIBS spectrum also shows some emission lines that could be related to presence of impurities such as titanium. In addition, LIBS reveals the presence of other elements such as calcium, sodium, etc. which could appear as they are present in the environment. In a similar way, the environmental oxygen nitrogen or hydrogen are mainly responsible for the signal observe for these elements although in the case of oxygen, an important contribution comes from the alumina and silica.

### **Fig. 2**

**Fig. 3** shows a detailed plot of the emission lines corresponding to Al I (265,4 nm) and Al I (266,1 nm) of untreated HNTs and chemically etched HNTs with different acids. As it can be seen, after the acid treatment, a decrease in the signal of both spectral lines is detected but this decrease is more pronounced for HNTs chemically etched with sulphuric acid. Regarding the etching treatments with acetic and acrylic acids, the intensity of the Al I lines is slightly reduced thus giving evidences of the mildest conditions compared to sulphuric acid. These results are in total agreement with the previous exposed **XRF** and TEM results.

### **Fig. 3**

LIBS technique allows also quantitative analysis, so that it is possible to use LIBS to characterize the effects of the different acid etching treatments on the chemical composition of HNTs, as well as the presence of impurities due to the high sensitiveness. With the aim of revealing the amount of aluminium in HNTs and the effects of the selective etching on the alumina interior layer, aluminium was analysed in a quantitative way from LIBS results. The Al I (265.4 nm) was selected for quantitative determination as it does not overlap with other nearest emission lines and

it offers an acceptable emission intensity for quantitative analysis. In addition, an emission line of a second element was used as internal pattern, to correct potential oscillations in the LIBS signal during measurements due to some factors such as small shot-to-shot pulse energy variations. The selected emission line was Si I (243.5 nm) as it does not show any interference and this line is placed near to the analytic line Al I (265.4 nm). An initial calibration was carried out by the standard addition method, leading to good linear correlation with  $r^2 = 0.992$ , with repeatability values for the calibration points in the line between 1.19% and 5.316% RSD ( $n = 3$ ). Once the aluminium concentration in untreated HNTs was assessed and the relationship between the emission intensity of LIBS and the actual aluminium concentration was established, chemically etched HNTs with different acid treatments were quantitatively analysed. The obtained results are summarized in **Table 3** which shows the average values obtained from three independent replicates. As it can be seen, the aluminium content in untreated HNTs is 25.5%. After the acid treatments, the aluminium content decreases for all three acid treatments but once again, it is the sulphuric acid which gives the minimum aluminium content of 18.9% due to the aggressive etching phenomena on the interior alumina layers. With regard to the aluminium content for HNTs chemically etched with acetic and acrylic acid, it reaches values of 24.1% and 22.6% respectively thus giving evidence of the milder effects of these two organic acids compared to sulphuric acid. **Table 3** also shows the ratio between the Si I (243.5 nm) and the Al I (265.4 nm). As it can be seen, as the aluminium content decreases, the Si/Al ratio increases as previously observed by **XRF**. The obtained results by using the LIBS technique are in total agreement with those obtained by **XRF** analysis. Both techniques indicate the strong effects that sulphuric acid etching has on HNTs, compared to acetic and acrylic acid.

**Table 3.** Aluminium content of untreated and chemically etched HNTs with different acids as obtained by quantitative analysis using LIBS.

Sample	Al (%)	Si I (243.5nm)/Al I (265.4 nm)
HNTs	25.5 ± 0.1	1.04 ± 0.18
ACR-HNTs	24.1 ± 0.4	1.10 ± 0.05
ACE-HNTs	22.6 ± 0.5	1.17 ± 0.06
SUL-HNTs	18.9 ± 0.4	1.43 ± 0.15

Although a slight difference regarding the aluminium content between XRF and LIBS can be observed, it is important to remark that both techniques show similar compositions for untreated and chemically etched HNTs. In particular, XRF results offer similar Si/Al ratios for untreated HNTs and HNTs subjected to mild treatment with weak acids (acetic and acrylic). On the other hand, LIBS has revealed an increase in the Si/Al ratio for all acid-treated HNTs which could indicate that LIBS is more sensitive than XRF for this analysis.

### 3.3. Effect of selective acid treatment on the porous texture of HNTs.

**Fig. 4** shows the corresponding nitrogen adsorption-desorption isotherms of untreated and selectively etched HNTs. As it can be seen, all four samples show a type IV isotherm according to IUPAC classification [44], which is typical of a mesoporous structure. The hysteresis loop of these samples is similar to type H3, which is typical of agglomerates of plate-like particles containing slit-shaped pores [43]. The hysteresis loops can be observed in the  $P/P_0$  range comprised between 0.4 to 1, which is associated with the capillary condensation in mesopores (pore width: 2–30 nm). **Table 4** summarized the BET values and the pore volume of untreated and chemically etched HNTs. As it can be seen, untreated HNTs show a BET surface area of 52.9  $\text{m}^2 \text{g}^{-1}$  and a pore volume of 0.146  $\text{cm}^3 \text{g}^{-1}$ . After the acid treatment, a remarkable increase in the BET surface area and the pore volume is detected, being the sulphuric acid treatment which leads to the highest values. Specifically, the BET surface area increases up to values of 132.4  $\text{m}^2 \text{g}^{-1}$  and a pore volume of 0.308  $\text{cm}^3 \text{g}^{-1}$ . This increase in both the surface and the pore volume is

directly related to the selective dissolution of the octahedral  $\text{AlO}_6$  layers with the subsequent increase in the average diameter of the lumen. Several authors such as Wang *et al.* [36], Zhang *et al.* [40] or Belkassa *et al.* [45] have reported that an increase in the acid concentration or the treatment time also gives an increase in the surface area and the pore volume for HNTs. For these reasons, selective etching of HNTs with acids is very interesting for new applications such as drug supporters, enzyme carriers, and selective adsorbents.

**Fig. 4**

**Table 4.** BET surface area and total pore volume of untreated and chemically etched HNTs with different acid treatments.

Sample	BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
HNTs	$52.9 \pm 0.8$	$0.146 \pm 0.004$
ACR-HNTs	$58.5 \pm 0.7$	$0.176 \pm 0.005$
ACE-HNTs	$60.1 \pm 0.9$	$0.195 \pm 0.004$
SUL-HNTs	$132.4 \pm 10.5$	$0.308 \pm 0.018$

**Fig. 5** shows the BJH pore size distribution obtained from the data collected from the desorption isotherm of the different HNTs. As it can be seen, untreated HNTs show two pore sizes distributions. One with an average pore size of 2 nm which is attributed to the small internal and external pores [46]. The second distribution is centred at about 6-9 nm and is mainly related to the lumen [47]. Such pore size distribution corroborates the mesoporous structure of HNTs. After the different acid treatments, some changes in the pore size distribution can be observed. Specifically, the peak centred at 2 nm is moved to 4 nm which suggests an increase in the average pore size. With regard to the peak centred at 6-9 nm it is also detectable a displacement towards higher values of 12 nm due to the selective removal of  $\text{Al}^{3+}$  cations from octahedral layers contained in HNTs [48]. It is worthy to note that HNTs treated with sulphuric acid show additional peaks through a wide range this giving evidences of a heterogeneous porosity inside HNTs which



is directly related to the aggressiveness of this acid treatment. Another interesting finding is macropore formation by acid treatment with sulphuric and acetic acid. This is mainly due to the penetration of protons into the clay mineral layers and attack to the structural hydroxyl groups resulted in the dehydroxylation and a successive leaching of the  $Al^{3+}$  ions from the octahedral layers, this produces a selective destruction of some layers and/or fragments which are responsible for the formation of holes inside de halloysitic matrix with the subsequent formation of macropores. [43, 45].

### Fig. 5

#### 3.4. Effect of selective acid treatment on the thermal stability of HNTs

Fig. 6 shows the TGA curves (Fig. 6a) and their corresponding derivative curves (DTG) (Fig. 6b) for untreated and chemically etched HNTs with different acid treatments. Two main weight loss stages can be identified for all samples. The first weight loss is comprised between 30 °C and 100 °C and this is related to desorption of the water that is physically adsorbed onto HNTs surface as well as desorption of the interlayer water [49]. These water molecules are weakly linked to HNTs and can be removed easily at relatively low temperatures. It is possible to observe that the weight loss in this stage is higher for HNTs treated with sulphuric acid, which suggests that these HNTs contain more adsorbed water due to the porous structure that sulphuric acid provides [43] as well as the highly hygroscopic nature of the sulphuric acid residues in comparison with other acids. The second and highest weight loss can be observed in the 400 – 600 °C (with a DTG peak at about 500 °C) and is directly related to the dehydroxylation of the structural Al-OH groups of halloysite [49-51]. As it can be seen, the weight loss in this stages highly depends on the acid treatment. HNTs subjected to etching with sulphuric acid show less weight loss compared to HNTs subjected to acetic or acrylic acid treatments. This could be related to the fact that hydroxyl groups present in the octahedral layer of  $AlO_6$  are removed together with the  $Al^{3+}$  solution [40]. This lower weight loss gives evidences of the aggressiveness of the sulphuric acid treatment which is responsible for a higher removal of Al-OH groups in comparison to the other

acid treatments. The weight loss in this second stage is similar for untreated HNTs and HNTs subjected to a mild etching process with acetic and acrylic treatments.

### Fig. 6

#### 3.5. Effect of selective acid treatment on the crystal structure of HNTs

The effect of the acid treatment was also observed on the crystal structure of untreated and chemically etched HNTs. Fig. 7 shows the XRD patterns of untreated HNTs and chemically etched HNTs with different acid treatments. XRD patterns of untreated HNTs are in total agreement with previously reported results [50, 52, 53]. As it can be seen, a diffraction peak appears at  $2\theta = 11.8^\circ$  which corresponds to  $d_{001}$  diffraction planes with a basal spacing of 0.754 nm. An additional peak is observed at  $2\theta = 24.8^\circ$  which can be attributed to the  $d_{002}$  diffraction plane with a basal spacing of 0.358 nm. These two main diffraction peaks in untreated HNTs indicate that these HNTs correspond to a dehydrated halloysite structure (halloysite-7Å) [54]. The intense diffraction observed at  $2\theta = 20.0^\circ$ , which is attributed to the  $d_{020}$  plane with a basal spacing of 0.444 nm, confirms the tubular structure of halloysite [55]. The diffraction peak at  $2\theta = 26.6^\circ$ , corresponds to quartz ( $\text{SiO}_2$ )  $d_{020}$  plane in halloysite [56]. As it can be seen, all chemically-etched HNTs show similar XRD patterns to untreated HNTs which indicates that the crystal structure is maintained after the acid treatments. Wang *et al.* [36] and Saklar *et al.* [57] also observed as the crystalline structure of HNTs was not affected after the acid treatment with HCl and  $(\text{COOH})_2$ . Despite this, some authors reported the disruption of the crystalline structure after acid treatment with more aggressive conditions as Zhang *et al.* [40] or Belkassa *et al.* [45] concluded. The diffraction peak at  $d_{001}$  is not shifted to lower angles which indicates that the acid molecules are not inserted between different layers. This fact corroborates that the chemical attack proceeds from the lumen (internal alumina layers) to the external walls [35]. It is worthy to note that the acid treatments give a decrease in the intensity of the  $2\theta = 11.8^\circ$  peak as a consequence of the dealumination process. This decrease is directly related to the increase in intensity of the silica

$d_{011}$  peak [35, 40, 58]. These phenomena are more pronounced for HNTs treated with sulphuric acid thus giving clear evidences of the high aggressiveness of sulphuric acid compared to acetic or acrylic acids.

**Fig. 7**

#### **4. Conclusions**

The present work assesses the effects of different acid treatments on the morphology and chemical composition of HNTs. Acid treatment is an effective way to selectively modify HNTs for different purposes. Chemical treatment with strong acids such as sulphuric acid leads to a highly aggressive etching on HNTs characterized by a highly porous structure and partial nanotube decomposition. The specific surface area of HNTs modified with sulphuric acid is of about  $132.4 \text{ m}^2 \text{ g}^{-1}$  which indicates the potential of HNTs in catalysis applications. On the other hand, the selective etching by using weak acids such as acetic and acrylic acid, leads to a noticeable increase in the lumen (inner hollow diameter) in HNTs which has a positive effect on the overall potential of HNTs as carrier for different loads. As per the results, the lumen diameter changes from  $13.8 \text{ nm}$  up to  $18.4$  and  $17.1 \text{ nm}$  for acetic and acrylic acid treatments respectively which lead to an increase in the carrying volume of  $77.8$  and  $53.5\%$  respectively. The results obtained in this work, widens new and interesting applications for natural nanotubes from halloysite by selective etching with different acids to obtain tailored morphologies and properties.

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## Figure captions

**Fig. 1.** TEM images and plot representation of the lumen diameter distribution of HNTs subjected to chemical etching with different acids, a) untreated, b) sulphuric acid, c) acetic acid and d) acrylic acid.

**Fig. 2.** LIBS spectrum of untreated HNTs showing the main emission lines.

**Fig. 3.** Aluminium emission lines obtained in LIBS analysis of untreated and chemically etched HNTs with different acid treatments.

**Fig. 4.** Nitrogen adsorption isotherms of untreated and chemically etched HNTs with different acids.

**Fig. 5.** BJH pore size distribution of untreated and chemically etched HNTs with different acids.

**Fig. 6.** TGA (a) and DTG (b) curves for untreated and chemically etched HNTs with different acid treatments.

**Fig. 7.** XRD diffraction patterns of untreated and chemically etched HNTs with different acid treatments.