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Natural clays for CO_2 sequestration: study in the form of powder as previous stage before their use in structured filters

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Abstract: The potential application of some natural spanish clays in the retention of CO_2 was investigated. Temperature-Programmed Desorption experiments monitored by both thermogravimetry and mass spectrometry, combined with infrared spectroscopy, after treatments with CO_2 at r.t. under dynamic conditions were used to evaluate its interaction with the clays. This study was performed not only over the raw materials but also after cationic exchange with NaCl followed by intercalation of a polyalcohol dendrimer. Additionally, textural, structural and compositional characterization of the clays by means of N_2 physisorption, X-ray diffraction, SEM-EDS and granulometry was carried out. The results indicate that although the raw clays exhibit some intrinsic capacity to capture CO_2, this can be increased by further intercalation of the polyalcohol. Moreover, the strength of the CO_2 interaction and therefore the possibility of regeneration of the clays upon saturation can be modulated by their nature and the amount of dendrimer employed. Finally, after screening the powdered clays, those showing the best performance were selected to manufacture clay-based honeycomb monoliths, an advantaged design for applications which require treating high flows of polluted effluents. For this, both extrusion of clay doughs and deposition over a preformed clay-based honeycomb support by washcoating methods were considered.

Keywords: Air pollution control;carbon sequestration; clay; CO_2; honeycomb monoliths

1. Introduction

In the last few decades, CO_2 emissions have become a very serious problem worldwide that forces global community to adopt urgent measures. This is so because this gas is recognized as the major responsible of global warming and anthropogenic climate change due to its well-known greenhouse effect. Moreover, its atmospheric concentration keeps on increasing due to the large-scale burning of fossil fuels.

Many different technologies have been considered to reduce CO_2 release to atmosphere at large scale, such as injection into seas or burial inside deep saline aquifers, exhausted natural gas or oil wells and non-exploitable coal seams. Although capacity of these reservoirs to capture CO_2 throughout the planet is enormous, their use imply high costs of transportation and might have collateral effects such as those derived from ocean pH change. In this sense, CO_2 sequestration in solid sorbents is being given recently the most attention as their portable condition may offer the advantage of in situ treatment of polluted effluents. In any case, for any practical application of these solid CO_2 sorbents, factors like working temperature, sorption capacity, selectivity, durability, and the cost should be taken into account.

In the above context, clay materials have many advantages compared with other adsorbents such as those based on solid amines, carbons, graphite/graphene, zeolites, metal-organic frameworks, silica, polymers, alkali metal carbonates, immobilized ionic liquids, boron nitrides, MgO, CaO and alkali zirconates or silicates. Clay materials have high surface area, high mechanical and chemical stability. In addition, clays have low cost and relative easiness in availability, regeneration and production in large enough quantities [1].

In spite of the fact that the use of clays for CO_2 capture has also attracted some attention recently, their use in the form of honeycomb monoliths for this application is still surprisingly missing [2,3]. Nevertheless, if high volumes of gaseous effluents containing low CO_2 concentration had to be treated, such design would be better to ensure low pressure drop [4]. Furthermore, honeycomb monolithic filters, being unitary structures, would facilitate both handling and replacement upon saturation.

This work is conceived as preliminary screening of several natural clays in the adsorption of CO_2, both as received and after further modification as suggested by previous publications, either by cationic exchange [5,6] or intercalation of a polyalcohol dendrimer [7,8]. In a second step, the clay showing the best performance is selected to prepare clay-based honeycomb monoliths, both by extrusion of a paste containing it and by washcoating a preformed honeycomb support with a stable slurry obtained from the chosen clay.

2. Experimental

2.1. Samples preparation

In this work five different natural clays have been studied. Four of them, named Aguila, Archidona, Esquivias and Yuncos, were provided by Süd-ChemieEspaña, and proceeded from different deposits located at the centre and south of Spain. They consisted of sepiolitic, pure, kerolitic and calcic montmorillonites, respectively. The last one, called Argi, having a high content of quartz (57 wt%) [9], was given by VICAR S.A., and came from deposits at the east of Spain. Like the rest, except Aguila which presented the form of granules and thus was crushed before any use, it was received as a fine powder.

For the cationic exchange, 3 g of each clay were mixed with 0.5 g of NaCl and 100 ml of distilled water, and heated at 85 ºC with continuous stirring (200 rpm) for 150 min. After filtering, the excess of chlorine was eliminated by repeated washing, the resulting powder being finally dried at 60 ºC overnight.

Further intercalation of the clays was performed by using a bulky hyperbranched H-30 Boltorn polyol dendrimer. In this case, 2 g of each clay were mixed with 12 mg of polyalcohol in a 1:1 ethanol/water solution so to obtain a final 6% by weight content of the dendrimer. The mixture was gently dried overnight (35 ºC) till thorough solvent evaporation. Hereafter resulting samples were called by their name followed by H-30 acronym.

2.2. Characterization techniques

Textural characterization was performed by means of N_2physisorption at -196 ºC using a Micromeritics ASAP2020 instrument. For this analysis the clay samples were pre-evacuated at 150 ºC for 1 h. Specific surface area was measured by the BET method. Total pore volume (V_p) was calculated from the amount of nitrogen adsorbed at relative pressures around 0.99. Pore size distribution and pore mean size diameter were determined by BJH method from the adsorption branch of the isotherms.

X-ray diffraction (XRD) studies were carried out in Bruker diffractometer, D8 Advance 500 model. The diffractograms were recorded using Cu Kα radiation. For the study of the fresh clays the 2θ angle ranged from 2º to 95º, with a step of 0.05º and a counting time per step of 20 s. For the modified samples 2θ ranged from 1.5º to 35º, with a step of 0.05º and a counting time of 10 s/step.

Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) compositional data were obtained using a QUANTA-200 scanning electron microscope equipped with a Phoenix Microanalysis System using a nominal resolution of 3 nm.

The granulometric study was carried out using a Mastersizer 2000 granulometer from Malvern Instrument, operating with laser diffraction. Typically, around 100 g of solid were dispersed in 20 ml of water. A few drops of the solution prepared were added to the sample chamber until getting 10-15% of obscuration. Record time was 12 s and laser intensity ranged from 77 to 80 %. To ensure reproducibility of the measurements, results were estimated in each case as the average of three independent runs.

Fourier transform infrared (FTIR) spectra were obtained in a Bruker Alpha infrared spectrometer in the form of KBr pellets. Spectra were collected in absorption mode with a resolution of 4 cm^{-1} and with 16 scans. The pellets were prepared by mixing 95 mg of KBr with 5 mg of clay.

Thermogravimetric analysis (TGA) was carried out under air in a TA Q50 thermobalance using a heating rate of 10 ºC/min. To study the interaction with the CO_2 the experiments were performed in a TA Q600 thermobalance with the following procedure: 1) cleaning pretreatment consisting of heating at 10 ºC/min under He (40 ml/min) up to 150 ºC, keeping this temperature for 1h,and cooling down to r.t. at the same rate; 2) treatment with CO_2 (60 ml/min) for 1 h; and 3) Temperature-Programmed Desorption (TPD) by heating at 10 ºC/min under He (40 ml/min) up to 900 ºC. The same analysis was performed for selected samples in a Thermostar QMS 200 (Pfeiffer) mass spectrometer (MS).

3. Results and Discussion

3.1. Clays' characterization

First, TGA was used to know the thermal stability of the clays and to establish a cleaning pre-treatment before their interaction with CO_2. Figure 1 shows the results of this analysis. As can be seen, Aguila is the clay exhibiting the highest weight loss upon heating (mainly below 200 ºC) which suggests a high level of retained humidity, being consistent with its sepiolitic nature. In general, high temperature peaks in the derivative curves are indicative of structural changes of the clays. In this sense, all clays seem to be quite stable, minimum up to 400 ºC, so ensuring a wide operative window. Moreover, TGA curve of the polyalcohol (also included in Figure 1) allowed concluding that 150 ºC (under He flow for 1 h) is a temperature that can be sufficiently high to clean the surface of the clays while low enough to prevent polyalcohol decomposition before treating the clays with CO_2.

Surface compositional analysis by SEM-EDS analysis confirmed the inclusion of sodium in all the clays as consequence of the cationic exchange performed, with replacement of other ions initially present such as potassium, calcium, iron and titanium (Figure 2).

On the other hand, the study be means of X-ray diffraction confirmed the inclusion of the polyalcohol in the clay structure as consequence of the further intercalation process applied. With exception or Argi, significant changes in the diffractogram were observed, especially in the low angles region (Figure 3). According to literature [8], they are related to (001) crystallographic planes and can be attributed to insertion of the dendrimer in the interlamellar space.

Regarding the N_2physisorption study, the obtained isotherms (results not shown) revealed the mesoporous character of all the clays, with some contribution of micropores. Table 1 summarizes the main textural properties derived from their processing. With exception of Aguila, there is some decrease (8-35%) of the specific surface area upon the dendrimer intercalation. Other authors working with the same polyalcohol [8] observed similar results. In any case, the still relatively high values of S_{BET} (around 200 m^2/g for Esquivias and even higher for Aguila) are certainly promising for a further use of these modified clays as adsorbents after deposition by means of washcoating over low surface area structured supports.

SEM micrographs (Figure 4) show that in general the clays present the typical smectite flakes, previously reported for other bentonites [10], displaying different agglomerates of particles with heterogeneous size. The surface roughness and inter-particle/agglomerate void spaces, which may also contribute to porosity, are similar to those observed in other natural clays [11].

Finally, to evaluate the potential of extrusion of the clays for a further application in the form of honeycomb monoliths, a granulometric analysis of the powdered samples has been also performed. It is well-known that both properties are related, and that Argi (as received) exhibits a great capacity of extrusion [9]. In this sense, similarity of the granulometry between Aguila and fresh Argi clays (Figure 5) can be considered a promising result to extrude the former. Similar results were obtained with the rest of the clays.

3.2. Study of the interaction with CO_2

Figure 6 shows the results of the experiment followed in a thermobalance for the Aguila H-30 clay to study its interaction with CO_2 according to the procedure described in the experimental section. Similar profiles were obtained for the other clays investigated, both as received and after modification.

Analysis of the central part of this multi-step experiment (i.e. the weight gain during the treatment with CO_2) allowed estimating the amount of CO_2 adsorbed by the clays (Table 2). As can be noticed, Aguila and Esquivias were those showing highest capacity to capture CO_2, the former exhibiting an extra clear improvement after intercalation of the polyalcohol. Such amount is competitive with that reported for other clay materials [6]. On the contrary, there was a slight worsening of the performance in the rest of the clays. Moreover, changes in the amount of CO_2 adsorbed as consequence of the clay modification seemed to follow the same trend of those found in the specific surface area (see Table 1).

The effect of the polyalcohol intercalation on the CO_2 sequestrated can be easily visualized by comparing the derivative curves of the weight loss during the TPD (third step of the TGA experiment) of all the clays in the temperatures range (25-200 ºC), in which the signal can be only due to the CO_2 pre-adsorbed (Figure 7). Similar results were obtained by MS analysis. Also remarkable, further changes in upper regions of temperature (results not shown) suggested that the use or not of dendrimer and the amount included can also modulate the strength of the interaction of the clays with CO_2.

With the purpose of confirming this modulation effect, infrared spectra were also recorded for all the clays in three consecutive steps, as received (Fig. 8), doped with the polyalcohol and after the treatment with CO_2. Unfortunately, this analysis did not give more light as no significant changes were observed, most likely due to instrumental limitations. Certainly, the use of self-supported pellets, instead of KBr diluted, and of infrared cells to enhance sensitiveness and avoid contact with air, so preventing the atmospheric CO_2 interference, would help respectively.

4. Conclusions

In this work a screening of different natural clays in the form of powder to evaluate their further potential as CO_2 adsorbents in the form of honeycomb monoliths has been carried out.

The study showed that the raw clays without any modification are already able to capture CO_2. The amount retained was not high but it is significant and comparable with that previously reported for other clay-based [6] adsorbents. Aguila and Esquivias were those showing the best performance, while Argi appeared as the worst clay most likely due to its lower content in montmorillonite.

SEM-EDS and X-ray diffraction analyses confirmed that all the clays investigated can be widely exchanged with sodium chloride, and further modified by intercalation of Boltorn H-30 polyalcohol,

respectively. The clays also showed good textural properties as evidenced by N_2physisorption, which is a pre-requisite for any use as adsorbent. As above, Aguila and Esquivias exhibited the best behaviour and Argi the worst. Nevertheless, no direct and unique correlation seemed to exist between the textural properties of the clays and their intrinsic capacity to adsorb CO_2. This finding is consistent with other authors' observations [8].

Study of the CO_2-clay interaction by TPD experiments followed by both thermogravimetry and mass spectrometry suggested that modification of the clays served to modulate the strength of such interaction. This is a key property for regenerating the clays upon saturation or releasing the CO_2 when needed.

Regarding the effect of intercalation on the amount of CO_2 adsorbed, this doubled in Aguila while slightly decreased in the rest of the clays. Such evolution resembles that observed for the specific surface area of each clay.

Perhaps results could have been better by submitting the clays to purification [6-8] or acid treatments [12], nevertheless the scope of this work was to investigate the potential of natural clays to sequestrate CO_2 without pre-treatments that may imply high cost or long procedures. In this sense, the fact that some of the raw clays investigated (especially Esquivias and Aguila) captured CO_2 without any modification, besides presenting optimal textural and granulometric properties, makes them good candidates for the extrudibility studies that are necessary before honeycomb monolith manufacture can be faced [3].

Acknowledgment

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Table headings

Table 1Textural properties of the clay samples investigated, both fresh and doped with H-30 Boltorn polyol
Table 2 Amount of CO_2 adsorbed by the samples (mg CO_2/g clay) as estimated by thermogravimetric analysis

Figure captions

Figure 1 Thermogravimetric analysis of the fresh clays (left) and the polyalcohol used to modify them (right).
Figure 2 Results of SEM-EDS analysis for the fresh and Na-exchanged clays. Other elements (Si, O, Al, C) also present are not included for the sake of clarity. The arrows help to visualize the increase of Na content after the cationic exchange.
Figure 3 X-ray diffractograms of Aguila clay (taken as representative), both fresh and doped with H-30 polyalcohol. Appearance of peak at 23.7º in the doped sample is attributable to expansion of the interlamellar space in the montmorillonite fraction, so elongating the c lattice parameter.
Figure 4 SEM micrographs obtained for Aguila H-30 (left) and Argi H-30 (right), taken as representative of all the clays studied.
Figure 5 Particle size distribution in volume as obtained by granulometric study for Aguila (left) and Argi (right) clays.
Figure 6 Curves obtained for the Aguila H-30 clay taken as representative of the TGA experiments performed to study the interaction of the clays with CO_2. First part (up to approx. 200 min) corresponds to the cleaning pre-treatment under He (40 mil/min), second part (up to approx. 270 min) represents the treatment with CO_2 (60 ml/min), and third part (till the end) shows the subsequent TPD under He (40 ml/min).
Figure 7 Correlation between texture and adsorption capacity of the clays studied.
Figure 8 Derivative of the TGA curves during the TPD-CO_2 experiments.
Figure 9 Infrared spectra corresponding to fresh clays studied.

Table 1

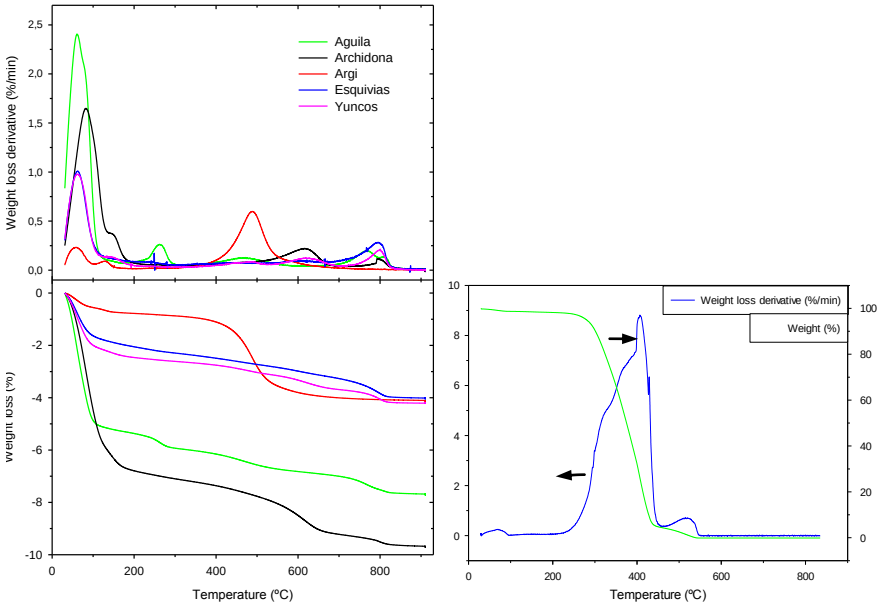
Sample	S_{BET} (m^2/g)	V_p (cm^3/g)[a]	V_{micro} (cm^3/g)[b]	D_p (nm)[c]
Aguila	123	0.129	0.025	6.6
Aguila H-30	242	0.280	0.048	7.3
Archidona	135	0.169	0.024	7.3
Archidona H-30	87	0.109	0.012	8.4
Argi	29	0.084	0.001	13.5
Argi H-30	22	0.112	0.002	15.7
Esquivias	257	0.224	0.048	5.2
Esquivias H-30	188	0.177	0.018	4.1
Yuncos	58	0.102	0.012	10.7
Yuncos H-30	53	0.066	0.004	5.0

[a]Estimated from the amount of nitrogen adsorbed at P/P_0=0.99
[b]Estimated by means of t-plot (Harkins-Jura) analysis from N_2physisorption data
[c]Determined from the adsorption branch of the N_2physisorption isotherm following the BJH method

Table 2

Clay	Fresh	H-30 doped
Aguila	11.4	19.2
Archidona	6.2	6.2
Argi	1.8	1.5
Esquivias	11.5	10.7
Yuncos	5.6	4.1

Figure 1



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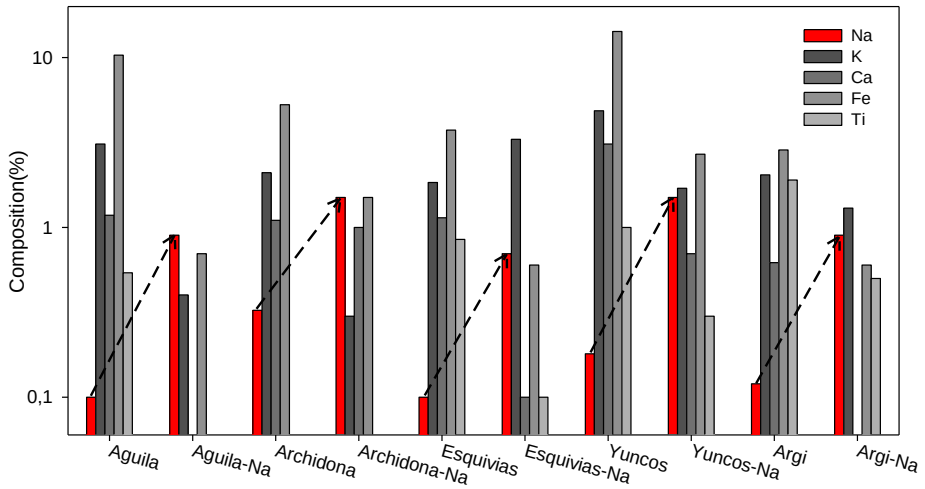

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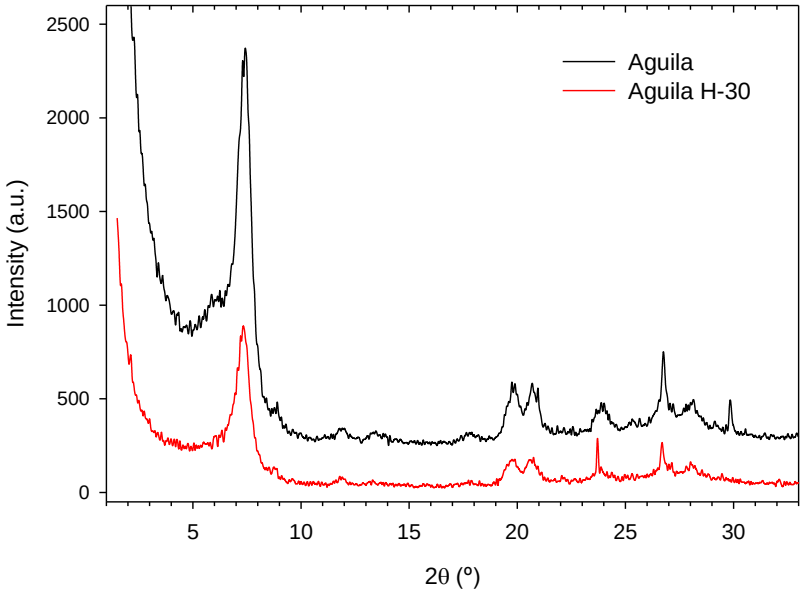

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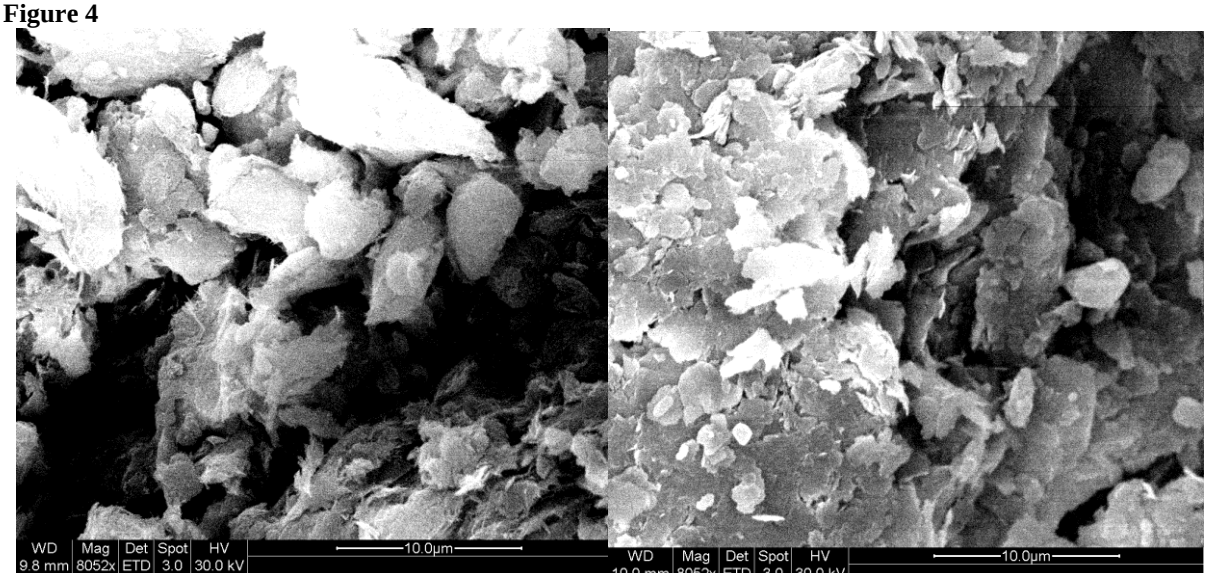


Figure 5

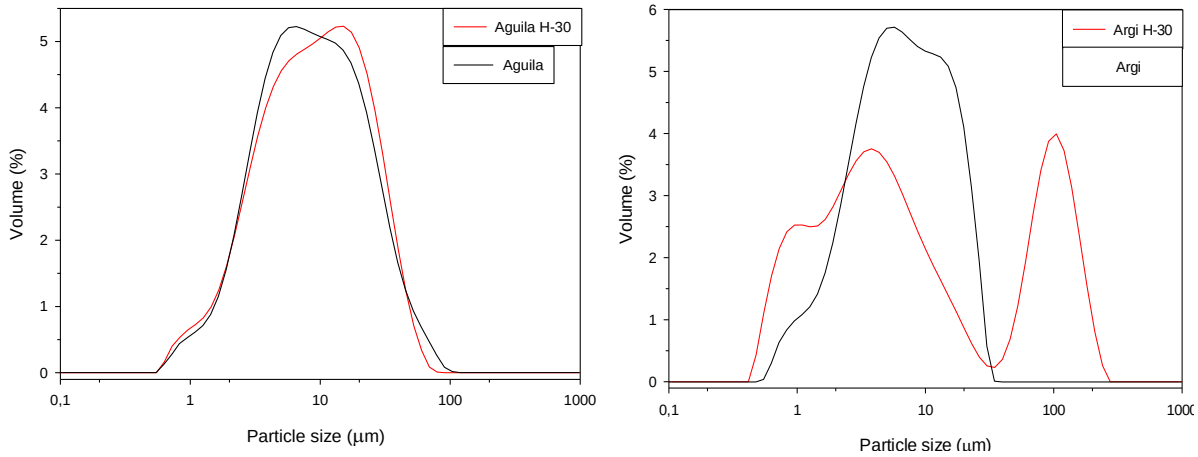
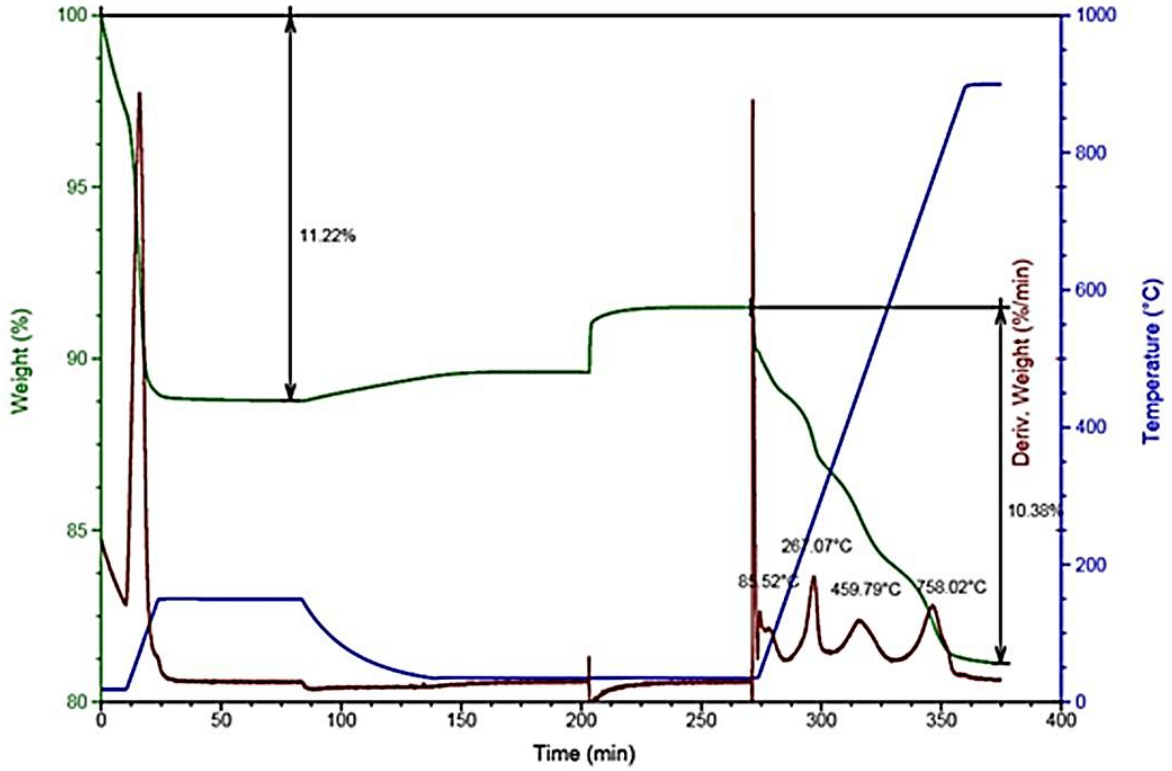


Figure 6



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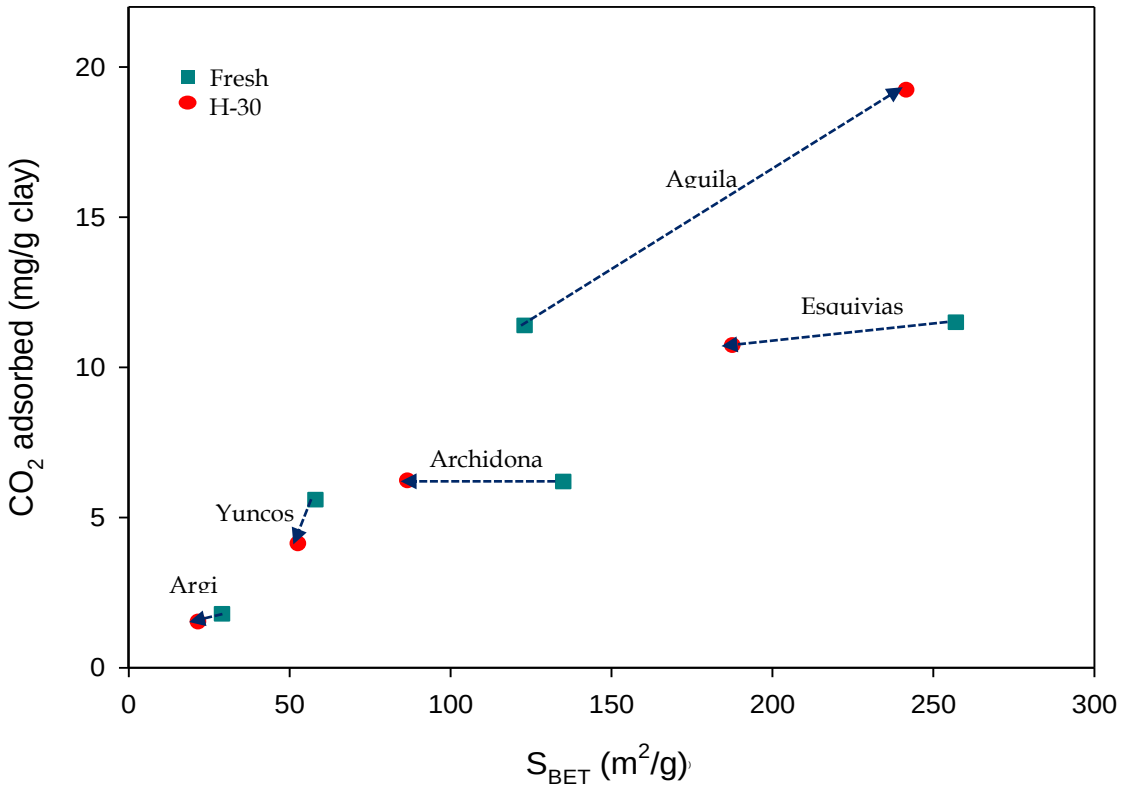

Figure 8

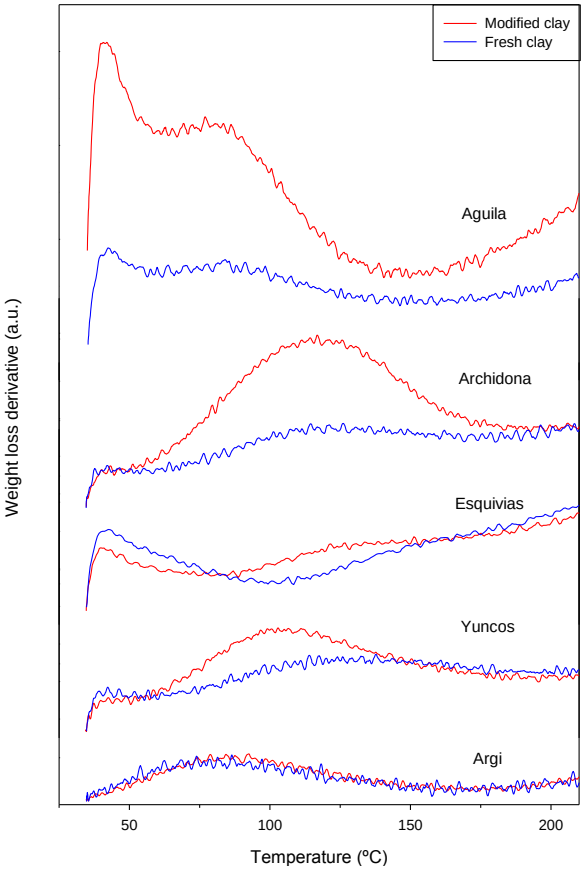

Figure 9