

# CO<sub>2</sub> adsorption on amine-functionalized clays

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## **Abstract**

Carbon capture using amine-modified porous sorbents is one of the main proposed technologies to reduce the CO<sub>2</sub> atmospheric concentration. In this work, a wide series of inexpensive clays have been selected to assess their role as supports of amine-containing sorbents for CO<sub>2</sub> capture. Montmorillonite, bentonite, saponite, sepiolite and palygorskite have been hydrated and functionalized by three routes: (a) grafting with aminopropyl (AP) and diethylenetriamine (DT); (b) by impregnation with polyethyleneimine (PEI); and (c) by double functionalization by impregnating previously grafted samples. XRD, FTIR and N<sub>2</sub> adsorption-desorption analyses along with nitrogen content and CO<sub>2</sub> adsorption properties (thermogravimetry and fixed bed) have been evaluated for bare and functionalized clays. Under dry conditions (45 °C, 1 bar), grafted and impregnated samples yielded CO<sub>2</sub> uptakes as high as 61.3 and 67.1 mg CO<sub>2</sub>/g ads (for Sepi-DT and Paly-PEI, respectively), with the latter being the best performing sample in terms of CO<sub>2</sub> uptake. On the contrary, double-functionalized samples displayed poor CO<sub>2</sub> adsorption properties, probably due to pore-blocking problems related to their high organic loading. The presence of 5 % H<sub>2</sub>O in the feed gas resulted in CO<sub>2</sub> uptake increments from 17 to 27 %. The adsorption performance of AP, DT and PEI containing samples was maintained after three adsorption-desorption cycles.

**Keywords:** *CO<sub>2</sub> capture, clays, amine groups, grafting, impregnation*

## 1. Introduction

Current human activities involve a continuous increase of global greenhouse gas concentration, mainly due to the use of fossil-fuels as energy resource. As a consequence, atmosphere and oceans have undergone an unequivocal warming, as pointed out by the Intergovernmental Panel on Climate Change (IPCC) [1]. In addition, the global temperature of the Earth is very likely to increase at least an additional 1.5 °C during the 21st century. Since CO<sub>2</sub> is considered the main responsible of global warming due to massive emissions from different human activities, it is crucial to minimize its release to the atmosphere. Energy efficiency and renewable energies are essential but not enough to fulfill this objective. Therefore, carbon capture, storage and utilization (CCSU) is also necessary [2,3].

Presently, the technologies established to capture CO<sub>2</sub> from large stationary sources, such as thermal power stations or cement plants, are based on the selective CO<sub>2</sub> absorption. Aqueous solutions of amines such as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA), among others, are commonly used. However, absorption exhibits important drawbacks, e.g. high rate of equipment corrosion, amine loss due to evaporation [4] and, mainly, high energy consumption during solvent regeneration [5]. Therefore, it is desirable the study of new strategies to capture CO<sub>2</sub> from flue gas.

In this context, adsorption on solid materials is considered an attractive alternative and, consequently, much effort has been made in order to develop appropriate adsorbents. Materials are generally selected in terms of: (i) low-cost of raw materials, (ii) low heat capacity, (iii) fast kinetics, (iv) high CO<sub>2</sub> adsorption capacity, (v) high CO<sub>2</sub> selectivity and (vi) thermal, chemical and mechanical stability. A large variety of solid adsorbents have been investigated, including zeolites, activated carbons, metal oxides, hydrotalcite-like supports, metal organic frameworks (MOFs), and polymers [6–9].

Since amines can selectively react with carbon dioxide [10–12], the modification of porous materials incorporating amino groups was proposed. Three main functionalization methods have been developed: impregnation of amines onto porous supports (class 1), formation of covalent bonds between the porous surface and amine-containing molecules (class 2) or in-situ polymerization (class 3).

Class 1 materials are solids loaded with any kind and amount of organic molecules with the only limit of the available pore volume. However, the accessibility of the amines is far from optimum when a considerable extent of the pore volume is filled. This technique has been extensively studied, with polyethyleneimine (PEI) being the main functionalization agent [13–17]. Class 2 materials present amines covalently bonded to the porous surface, and their accessibility is generally much higher. Nevertheless, the maximum amount that can be incorporated by grafting is restricted by the available specific surface area and the surface concentration of silanol groups. Mainly, three organosilane molecules have been used [18–20], containing one, two or three amino groups in their structures: aminopropyl (AP), ethylenediamine (ED), and diethylenetriamine (DT). Finally, class 3 materials are obtained by in-situ polymerization of aminated-monomers on the support surface. The main advantages of this class of adsorbents is the combination of high amino loadings with the stability given by covalent bonds to the surface [6,7].

Despite the extensive research regarding amine molecules and functionalization techniques, the cost of these CO<sub>2</sub> adsorbents is still medium-high [7,21]. Consequently, many research groups have recently studied low cost solid materials for CO<sub>2</sub> capture. Some of these groups have used industrial [22], agricultural [23], and domestic wastes [24], while others have considered inexpensive raw materials such as silicates [25], cellulose [26] or clays [27–29].

Clay minerals are a potential choice since they are inexpensive and abundant. Clays are hydrated aluminum phyllosilicates naturally formed through hydrothermal alteration of rocks. Generally, their structure is constituted by tetrahedral silicate sheets and octahedral hydroxide sheets arranged into layers. The structure of clays can also contain variable amounts of a wide variety of cations [30]. Due to their low price and moderated porosity, clay materials have been proposed as supports for commercial CO<sub>2</sub> capture, mainly montmorillonite [27,31–39], kaonilite [29] and bentonite [28,40]. Prior to amine loading, clays can be subjected to acid treatments in order to improve their textural properties by achieving higher pore volumes and surface areas than those of the raw materials. For example, the CO<sub>2</sub> uptake of un-modified kaolinite [29], bentonite [34,41], montmorillonite and smectite [42] ranged from 0 to 9.4 mg CO<sub>2</sub>/g ads (25 °C, 1 bar) and increased to 3.4-15.7 mg CO<sub>2</sub>/g ads after acid-treatments [29,42]. Azzouz et al. synthesized different montmorillonite samples intercalated with polyol dendrimers at different proportions (0.5-3 wt.%), leading to organoclays with physicochemical features combining those of the clay support and the organic moiety. The CO<sub>2</sub> uptake observed for these materials ranged between 22 and 110 mg CO<sub>2</sub>/g ads [27]. Except for this result, CO<sub>2</sub> uptakes were quite low despite modification efforts.

Song and co-workers loaded polyethylenimine (PEI) [39] and tetraethylenepentamine (TEPA) [40] onto several clays previously subjected to acid treatments. Results showed an optimum organic loading of 50 % in terms of both CO<sub>2</sub> net uptake and amine efficiency, measured as mol CO<sub>2</sub>/mol N. The influence of adsorption temperature was also studied, determining an optimum value of 75 °C for both PEI and TEPA. The adsorption of simulated flue gas (15 % CO<sub>2</sub>, 4.5 % O<sub>2</sub> balanced with N<sub>2</sub>) at 1 bar and 75 °C yielded CO<sub>2</sub> uptakes of 110 and 130 mg CO<sub>2</sub>/g ads for PEI and TEPA-containing adsorbents, respectively.[39,40] When ca. 18 vol.% water was included in the gas mixture, CO<sub>2</sub> uptakes of 161 and 190 mg CO<sub>2</sub>/g ads for PEI and TEPA were respectively obtained.

Roth et al. modified montmorillonite by grafting with AP, by impregnation with PEI [43], and by impregnating previously grafted samples (AP-PEI). An optimum temperature of ca. 85 °C was found for the three materials, observing also a high selectivity to CO<sub>2</sub>. At 85 °C and 10 vol. % CO<sub>2</sub> (1 bar) gas uptakes of 60 mg CO<sub>2</sub>/g ads were achieved for clays treated with only one of the amine compounds while double-functionalized sample presented a CO<sub>2</sub> uptake of 75 mg CO<sub>2</sub>/g ads [43].

Recently, Vilarrasa-García et al. used bentonite to prepare porous clay heterostructures, achieving a maximum pure CO<sub>2</sub> uptake of 45 mg CO<sub>2</sub>/g ads after grafting with AP and of 64 mg CO<sub>2</sub>/g ads after impregnation with PEI (25 °C, 1 bar) [44].

Due to the advantageous use of clay materials for CO<sub>2</sub> adsorption in terms of low cost and easy manufacturing, five different clay materials have been selected in this work: bentonite, saponite, montmorillonite, sepiolite and palygorskite. These materials have been hydrated with water and subsequently functionalized by (a) grafting with aminopropyl (AP) and diethylenetriamine (DT); (b) impregnation with polyethyleneimine (PEI) and (c) double functionalization combining grafting and impregnation techniques. This work implies a novel study in terms of the wide range of clays considered and the use of several functionalization techniques and amines.

## 2. Experimental

### 2.1. Hydration of clay materials

Five raw clay materials were selected in this study: bentonite (NaAlSiO-OH-H<sub>2</sub>O), K10 montmorillonite ((Na,Ca)<sub>0.3</sub>(Al,Mg)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·xH<sub>2</sub>O), PFI-1 palygorskite ((Na,Al)<sub>5</sub>(Si,Al)<sub>8</sub>O<sub>20</sub>(OH)<sub>2</sub>·8H<sub>2</sub>O) provided by Süd-Chemie, Acros Inorganics and the Clay Minerals Society, respectively and both Spanish saponite (Mg<sub>3</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) and sepiolite Pangel S9 (Mg<sub>4</sub>Si<sub>6</sub>O<sub>15</sub>(OH)<sub>2</sub>·6H<sub>2</sub>O) provided by TOLSA. With the aim of expanding

their original structures, all the samples were hydrated by dissolving 1 g of clay in 10 g of water. After stirring the mixture under ambient conditions for 2 h, the resulting slurry was vacuum-filtered and then dried at 50 °C for 2 h. Hydrated clays were named as Bent, Mont, Paly, Sapo and Sepi.

## **2.2. Functionalization of clay materials**

### **2.2.1. Grafting**

Hydrated clays were functionalized by grafting with amino-containing organosilanes, concretely (3-aminopropyl)-trimethoxysilane and  $N^1$ -(3-trimethoxysilylpropyl) diethylenetriamine. These compounds, abbreviated as AP and DT, contain one and three amino groups in their structures, respectively. The synthesis method consisted in dispersing 1 g of the selected clay in 250 mL toluene, homogenising the mixture by magnetic stirring for 10 min. After that, 12 mmol of the desired organosilane was added per gram of the hydrated clay. The mixture was refluxed for 24 h, filtered under vacuum and dried at room temperature overnight. So-obtained grafted adsorbents were denoted as CM-AP and CM-DT, where CM is the raw clay material.

### **2.2.2. Impregnation**

Hydrated materials were also functionalized by incipient wetness impregnation with polyethyleneimine (PEI). Pure PEI was added dropwise over 1 g of clay to reach a final loading of 37 wt.% in the adsorbent. Impregnated samples were dried at room temperature for 24 h and named as CM-PEI, with CM being the corresponding unmodified clay material.

### **2.2.3. Double functionalization**

Double-functionalized adsorbents were obtained by performing grafting and impregnation procedures consecutively on the same material. Following a procedure recently reported, hydrated clays were grafted with AP or DT and then impregnated with PEI [45]. Grafting loadings were the same as the ones previously described. Nevertheless, in order to avoid support

saturation, the amount added by impregnation was reduced to one half and one fourth of the initial pore volume of the parent hydrated clays, leading to final PEI loadings of 15 and 7 wt.% respectively.

Double-functionalized adsorbents were denominated as CM-Grf-PEI ( $x$ ), where *Grf* is the grafted organosilane (either AP or DT) and  $x$  stands for the weight percent of PEI loaded.

### 2.3. Physico-chemical characterization

Adsorption-desorption nitrogen isotherms at 77 K were measured for all samples with a *Micromeritics Tristar 3000 analyzer*. Before the analysis, materials were degassed for 8 h in N<sub>2</sub> flux at 200 °C (clay minerals) or 150 °C (organic-functionalized materials). BET specific surface area was determined in the relative pressure range between 0.05 and 0.20 and the total pore volume was calculated at a relative pressure of 0.97. The microporosity was calculated by the t-plot method.

X-ray powder diffraction (XRD) patterns of the samples were obtained with a *Philips X'Pert-MPD* diffractometer using a CuK $\alpha$  monochromatic radiation.

The Fourier transform infrared (FTIR) spectra were recorded in the region 4000-400 cm<sup>-1</sup> in a *Varian 3100 FT-IR Excalibur Series* registering 64 scans. The samples were dispersed in to the KBr powder and compressed to form thin disks before analyses.

The extent of the functionalization methods was assessed by measuring the amount of organic matter incorporated in each adsorbent, namely nitrogen, with a *Vario EL III Elementar Analyzer System GMHB*.

*ACD ChemSketch* and *3D Viewer* software were used to draw minimum-energy structures of organosilanes in order to calculate their total length.



#### **2.4. Evaluation of CO<sub>2</sub> adsorption/desorption over functionalized clays materials**

Pure CO<sub>2</sub> adsorption-desorption tests were performed in a *VTI Scientific Instruments HVPA-100* apparatus at 45 °C, with pressure ranging from 0 to 6 bar. Isotherms were acquired after a 2 h degassing step at 110 °C and  $5 \cdot 10^{-3}$  mbar. Sievert method was used to obtain isotherm points, with two combined equilibration criteria: a pressure drop smaller than 0.2 mbar in 3 min or a maximum equilibration time of 50 min. The average deviation for this measurement was calculated for raw sepiolite to be 1.1 mg CO<sub>2</sub>/g ads.

Cyclic adsorption-desorption measurements were performed at 45 °C and 1 bar using a CO<sub>2</sub> diluted stream (80 vol.% N<sub>2</sub>, 15 vol.% CO<sub>2</sub>, 5 vol.% O<sub>2</sub>, dry basis) with an additional 5 vol.% H<sub>2</sub>O. A fix bed reactor (*PID Eng & Tech Microactivity-Reference*) coupled to a mass spectrometer (*Pfeiffer Vacuum QMG220*) was used with this purpose. Prior to each analysis, a pretreatment was carried out to remove moisture and adsorbed gases by increasing the temperature to 110 °C in 100 mL/min argon for 2 h. After that, the temperature was decreased to 45 °C and subsequently 100 mL/min of the analysis gas mixture was introduced. Breakthrough curves representing CO<sub>2</sub> concentration in the output stream against versus time were integrated to calculate the total amount of CO<sub>2</sub> adsorbed.

During cyclic adsorption studies, materials were regenerated after every adsorption step in a similar way as performed for the pretreatment (100 mL/min Ar at 110 °C for 2 h).

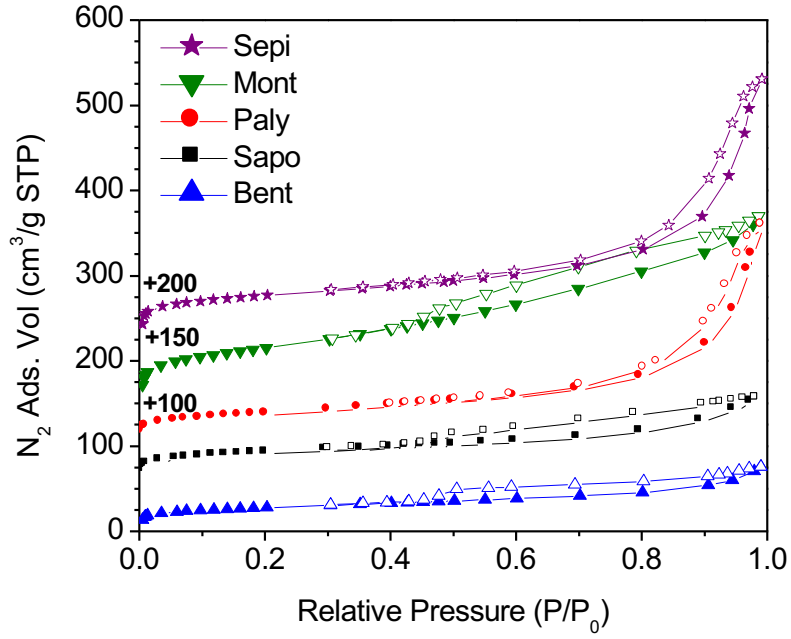
### 3. Results and discussion

#### 3.1. Clay minerals

N<sub>2</sub> adsorption-desorption isotherms of clay minerals are shown in Figure 1, with a summary of their main textural properties being listed in Table 1. Palygorskite and sepiolite presented isotherms that could be ascribed as Type II with H3 hysteresis loops [46], assigned to plate-like particles giving rise to slit-shaped pores [47]. Sepiolite isotherm is in agreement with other reported data presenting slight [48] or no [49] hysteresis loops.

Bentonite, saponite and montmorillonite showed H4 hysteresis loops, also related to slit-like pores [47]. These isotherms can be regarded as Type IV with heterogeneous pore size distributions. However it is not straightforward to ascribe these isotherms to conventional pre-defined types. For instance, montmorillonite isotherm has been previously defined both as Type II [50,51] and Type IV [52]. Besides, it is well known that non-polar adsorbates, such as N<sub>2</sub>, do not usually penetrate in the interlayer space of some clays [51], partially entering when clays are ion-exchanged with large cations such as Cs<sup>+</sup> or NH<sub>4</sub><sup>+</sup>.

The studied clays presented similar textural properties, with pore volumes varying between 0.11 and 0.42 cm<sup>3</sup>/g and surface areas in the range 107-274 m<sup>2</sup>/g. the contribution of micropores to these values is also listed in Table 1. It is interesting to note that sepiolite presents the highest contribution of micropores to both total pore volume (57 %) and surface area (19 %). Nevertheless, it must be noted that the conditions of N<sub>2</sub> and CO<sub>2</sub> adsorption tests are quite different. Thus, the textural properties described considering N<sub>2</sub> physisorption analyses are significantly different from the structure exposed to CO<sub>2</sub> molecules.



**Figure 1.** Nitrogen adsorption-desorption isotherms at 77 K of clay minerals. Some isotherms have been shifted vertically as shown in the legend.

**Table 1.** Textural properties and pure CO<sub>2</sub> adsorption uptake (45 °C, 1 bar) of clay minerals.

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{MICRO}}$ (m <sup>2</sup> /g)	$V_{\text{PORES}}$ (cm <sup>3</sup> /g)	$V_{\text{MICRO}}$ (cm <sup>3</sup> /g)	$q$ (mg CO <sub>2</sub> /g ads)
<b>Bent</b>	107	43	0.11	0.026	14.0
<b>Mont</b>	245	52	0.33	0.043	10.1
<b>Paly</b>	137	42	0.32	0.033	12.0
<b>Sapo</b>	151	69	0.16	0.040	15.4
<b>Sepi</b>	274	156	0.42	0.087	40.7

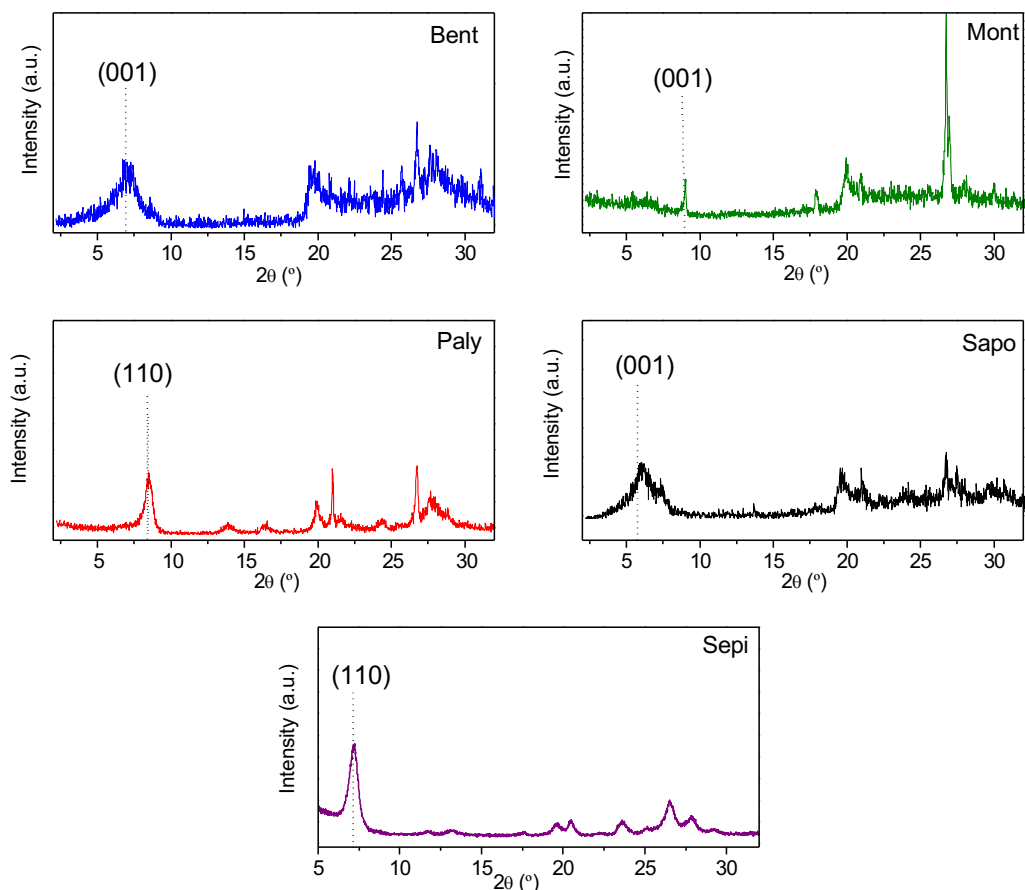
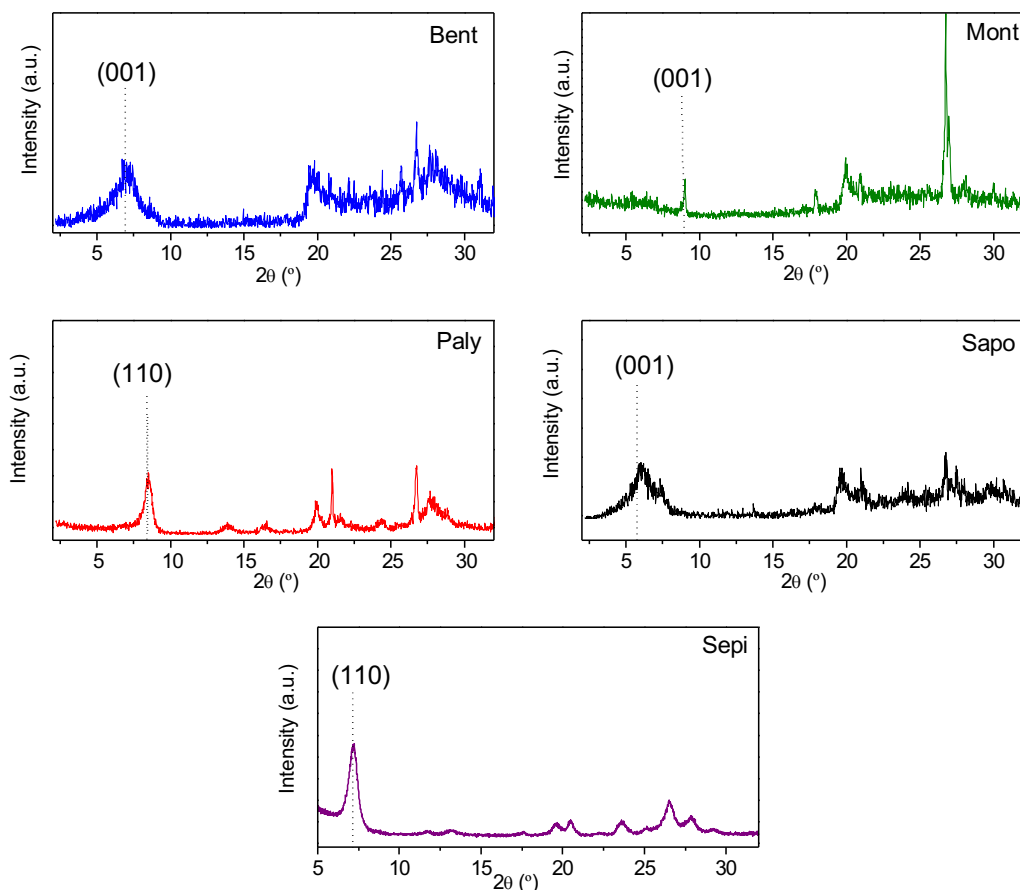


Figure 2 illustrates the XRD pattern of these clay minerals. The position of the characteristic reflection for a clay mineral varies between  $5.5^\circ$  and  $7.3^\circ$ , corresponding to the (1 1 0) plane for sepiolite and palygorskite and to (0 0 1) for bentonite, montmorillonite and saponite. These differences can be attributed to modifications in the interlayer spacing originated by compositional differences due to isomorphic substitutions [53,54]. A second group of reflections observed for  $2\theta$  values higher than  $10^\circ$  was related to the different crystal structure of each clay [55], as well as the presence of other minor components in the clays such as feldspars, carbonates, illite, dolomite and silica polymorphs (quartz and opal) [56–58].

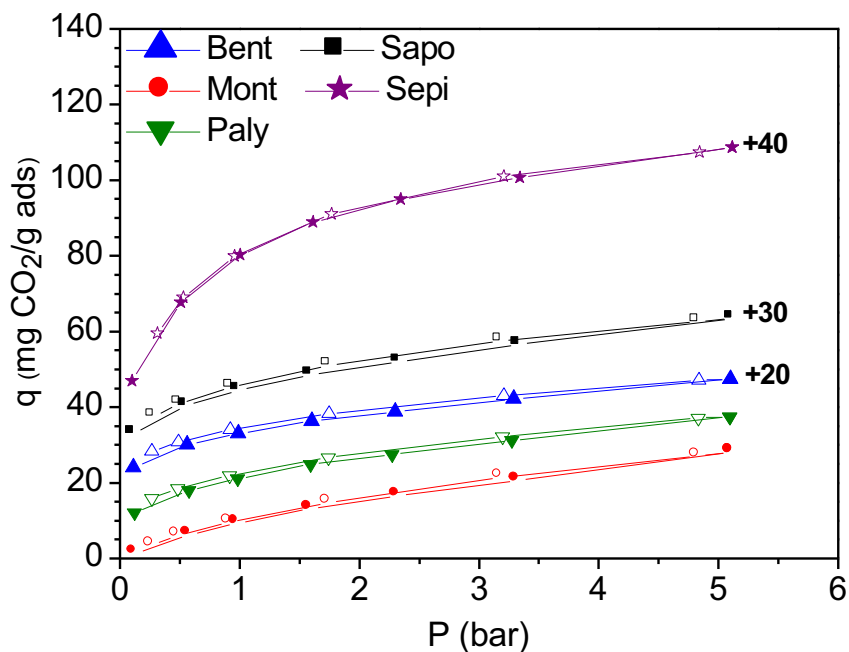


**Figure 2.** X-ray diffraction patterns of clay minerals.

Pure CO<sub>2</sub> isotherms were acquired at 45 °C for these samples (Figure 3). These isotherms presented small CO<sub>2</sub> uptakes at low partial pressures, a certain dependence of the adsorption uptake with the CO<sub>2</sub> pressure, and an almost complete reversibility of the process, as inferred from the overlapping of adsorption and desorption branches. These common features are characteristic of physical adsorption processes, which is in accordance with previously described trends for a number of non-functionalized physisorbents [59].

The CO<sub>2</sub> uptake values of these materials at 1 bar are listed in Table 1. As seen, there is no correlation between BET surface or pore volume with the amount of CO<sub>2</sub> adsorbed, contrarily with other findings for micro [60] or mesoporous [59] materials. CO<sub>2</sub> uptake values ranged between 10.1 and 40.7 mg CO<sub>2</sub>/g ads, with only sepiolite surpassing 15 mg CO<sub>2</sub>/g ads, probably

due to the considerable presence of micropores in its structure. These figures are too low to be considered in industrial CO<sub>2</sub> capture applications. In order to increase CO<sub>2</sub> uptakes, clay materials were modified by incorporating amino groups in their structures.



**Figure 3.** CO<sub>2</sub> adsorption-desorption isotherms at 45 °C for different clays. Some isotherms have been shifted vertically as shown in the legend.

### 3.2. Grafted materials

As expected, the textural properties of all clays grafted with AP and DT were reduced as a result of the organic functionalization. As an example, N<sub>2</sub> adsorption-desorption isotherms of palygorskite grafted with AP and DT are shown in

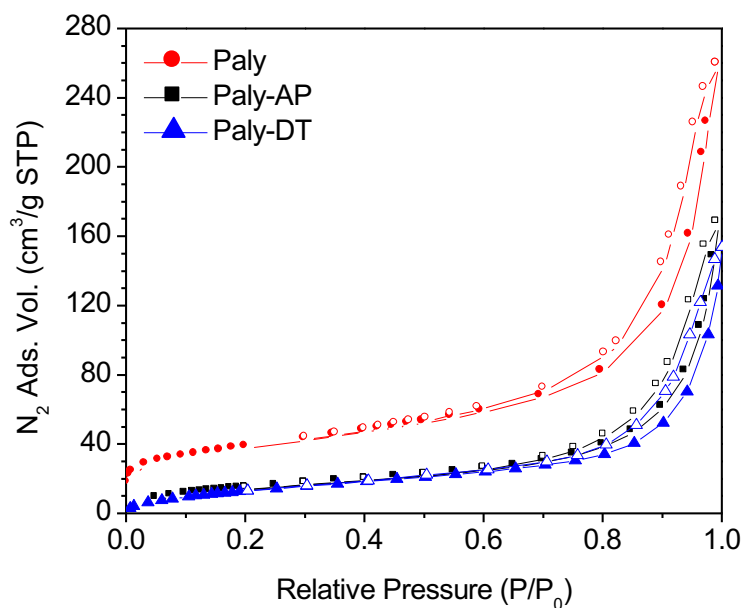
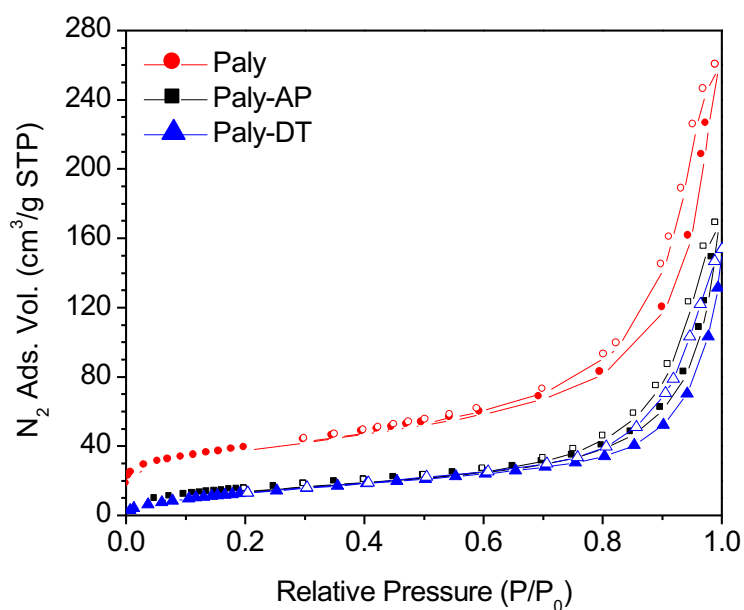


Figure 4. In this sample, BET surface was reduced from 137 m<sup>2</sup>/g for unmodified palygorskite, to 58 and 55 m<sup>2</sup>/g for AP and DT-containing samples, respectively. Similarly, pore volume decreased from 0.32 cm<sup>3</sup>/g to 0.19 and 0.16 cm<sup>3</sup>/g.



**Figure 4.** Nitrogen adsorption-desorption isotherms at 77 K of palygorskite-based grafted samples.

Table 2 shows the surface concentration of organosilane achieved by grafting as well as the organic nitrogen loaded. It is noticeable that the surface coverage with AP molecules (1.8-3.5 mmol silane/g ads) was much higher than that achieved with DT (0.5-1.2 mmol silane/g ads). This is coherent with previous findings reporting a negative effect of the silane length on the grafting process [61]. This fact has been ascribed to the arrangement of organosilanes, with their interaction with surface silanol groups leading to a kind of organic monolayer rather than to perpendicularly molecular disposition. Thus, taking into account that AP and DT organic chain length is of 8.5 and 13.6 Å respectively, it can be inferred that a given surface can accommodate more AP than DT molecules on account of its shorter chain length.

The total amount of nitrogen loaded for AP-materials ranged from 1.8 to 3.5 mmol N/g ads while their DT-grafted counterparts achieved values between 1.5 and 3.7 mmol N/g ads. Since DT moiety presents three amino groups in its structure and AP only one, this generally offsets the different molecule surface concentration [45].

**Table 2.** Nitrogen content and CO<sub>2</sub> adsorption properties at 45 °C and 1 bar for AP and DT-grafted clays.

Sample	mmol silane/ g ads	mmol N/g ads	q (mg CO <sub>2</sub> /g ads)	q <sub>m</sub> (mol CO <sub>2</sub> /mol N)
<b>Bent-AP</b>	2.8	2.8	43.2	0.35
<b>Mont-AP</b>	2.7	2.7	33.1	0.28
<b>Paly-AP</b>	1.8	1.8	37.9	0.48
<b>Sapo-AP</b>	3.5	3.5	35.0	0.23
<b>Sepi-AP</b>	2.8	2.8	43.8	0.31
<b>Bent-DT</b>	0.5	1.5	32.3	0.49
<b>Mont-DT</b>	1.1	3.4	50.0	0.33
<b>Paly-DT</b>	0.9	2.8	57.1	0.47
<b>Sapo-DT</b>	1.2	3.5	38.6	0.25
<b>Sepi-DT</b>	1.2	3.7	61.3	0.38

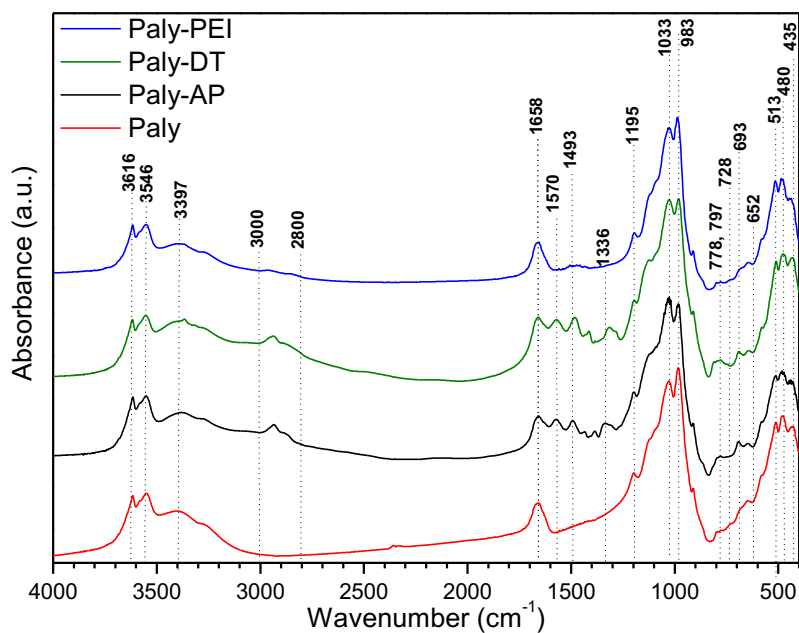
The FTIR spectra of a series of palygorskite samples are shown in Figure 5. Several bands can be observed in the unmodified clay. The bands at 3616 and 3546 cm<sup>-1</sup> can be assigned to the structural -OH groups of palygorskite (Mg-OH, asymmetric stretching) and water coordinated



to Mg (octahedral layer) [53], respectively. The broad band centered at  $3397\text{ cm}^{-1}$  corresponds to the stretching vibrations of both structural and free -OH groups. Similarly, the band at  $1658\text{ cm}^{-1}$  belongs to in-plane bending vibration of -OH groups.

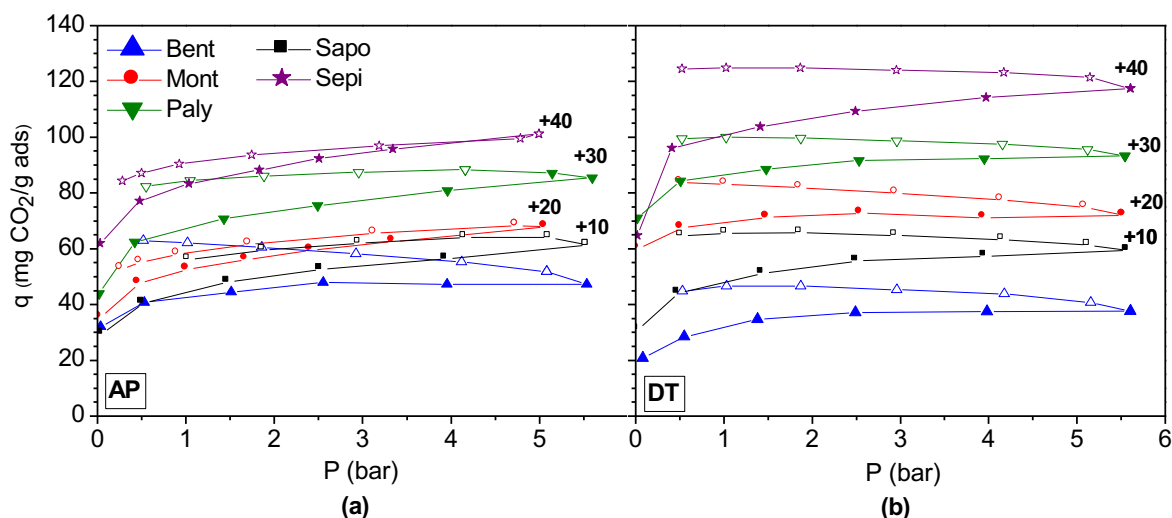
The intense peaks detected between  $900$  and  $1200\text{ cm}^{-1}$  as well as the one at  $480\text{ cm}^{-1}$  correspond to the overlapping of several contributions: out-of-plane and in-plane stretching vibrations of Si-O bonds of the tetrahedral silicate layers ( $1033$  and  $983\text{ cm}^{-1}$  respectively). Likewise, bands observed at  $778$  and  $797$ ,  $652$  and  $513\text{ cm}^{-1}$  correspond to bending vibrations of Si-O and Al-O bonds in octa- and tetrahedral silica-alumina layers in palygorskite [55]. The peak registered at  $435\text{ cm}^{-1}$  is ascribed to octahedral Si-O-Mg bending vibrations.

For AP and DT-functionalized palygorskite, apart from the above-described bands corresponding to the initial clay, some new contributions can be seen. Bands between  $2800$  and  $3000\text{ cm}^{-1}$  are assigned to symmetric and asymmetric stretching of C-H bonds in methylene and methoxy groups (-CH<sub>2</sub>-, -CH<sub>2</sub>-NH<sub>2</sub>, -O-CH<sub>3</sub>) due to organic groups loaded. The peaks observed at  $1570$  and  $1493\text{ cm}^{-1}$  are ascribed to N-H flexion vibration in primary and secondary amines and to -CH<sub>2</sub>- scissoring, respectively. Several additional peaks are observed between  $1195$  and  $1400\text{ cm}^{-1}$ , corresponding to H-N-H and H-C-H bending in the different bonds found in these molecules. The intensity all the bands assigned to grafted organosilanes was similar for DT-grafted palygorskite than in the case of AP.



**Figure 5.** FTIR spectra of unmodified, grafted and impregnated palygorskite.

CO<sub>2</sub> isotherms at 45 °C for grafted adsorbents are shown in Figure 6. They present common features, such as high CO<sub>2</sub> uptakes at low relative CO<sub>2</sub> pressures, a moderate increase of the adsorption capacity with the pressure and irreversibility of the process at the studied temperature. These trends are very similar to those found for other amine-grafted materials [16,45] and are in accordance with the contribution of chemisorption on amino groups to the overall CO<sub>2</sub> adsorption [62]. Besides, most desorption branches showed a slight increase ascribed to CO<sub>2</sub> diffusion limitations due to pore-structure restrictions, which is coherent with previous findings [63].



**Figure 6.** CO<sub>2</sub> adsorption-desorption isotherms at 45 °C of functionalized clays obtained by grafting with (a) AP and (b) DT.

CO<sub>2</sub> uptake ranged from 32.3 to 61.3 mg CO<sub>2</sub>/g ads at 45 °C and 1 bar (see Table 2), which is much higher than the values obtained by non-functionalized materials (10.1-40.7 mg CO<sub>2</sub>/g ads, Table 1). The total CO<sub>2</sub> uptake was also higher for DT-containing samples compared to AP ones, except for bentonite, due to the higher nitrogen loading previously discussed. In both cases, sepiolite reaches the highest CO<sub>2</sub> uptake, with values up to 61.3 mg CO<sub>2</sub>/g ads for Sepi-DT.

For amine-containing adsorbents it is also important to assess the CO<sub>2</sub>/N molar ratio, commonly considered as the adsorbent efficiency. CO<sub>2</sub> adsorption on amines follows a CO<sub>2</sub>:NH<sub>2</sub> reaction stoichiometry of 1:2 in the absence of moisture [10,11]. Thus, adsorption efficiency (defined as mol CO<sub>2</sub>/mol N) has a maximum theoretical value of 0.50 mol CO<sub>2</sub>/mol N due to the chemical reaction between CO<sub>2</sub> and amines. However, it is not unusual to register efficiency values around 0.50 mol CO<sub>2</sub>/mol N or even higher, especially for adsorbents with low amine-loadings, with the contribution of physical adsorption being high in these samples [64]. However, during efficiency calculation it is assumed that the adsorption uptake is only due to the presence of

amino groups, i.e. there is only chemical adsorption. Thus, high efficiency values for low-loaded samples (as some of the ones found in Table 2) have to be interpreted carefully.

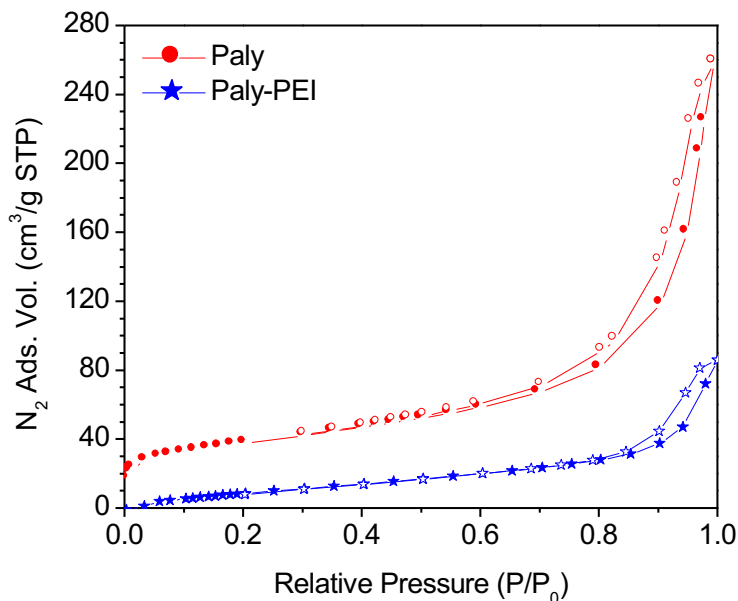
After the grafting treatment, AP and DT-containing adsorbents presented a wide range of amine efficiencies, from 0.23 to 0.48 mol CO<sub>2</sub>/mol N for AP and between 0.25 and 0.49 mol CO<sub>2</sub>/mol N for DT. Since these series are both in a wide range, they cover all the results typically found for grafted supports in pure CO<sub>2</sub> capture [6,7].

### **3.3. Impregnated materials**

Polyethyleneimine-impregnated adsorbents were characterized by N<sub>2</sub> adsorption-desorption, observing a reduction in their textural properties. Again, an example for palygorskite can be seen in Figure 7, whose specific surface area and pore volume decreased from 137 to 42 m<sup>2</sup>/g and from 0.32 to 0.11 cm<sup>3</sup>/g, respectively. These reductions are more marked than the ones observed for grafted materials, since both the organic amount loaded and PEI viscosity are higher compared to AP or DT-grafted samples.

The organic nitrogen loading ranged between 4.9 and 7.6 mmol N/g ads for PEI impregnation, surpassing the maximum value of 3.5 mmol N/g ads obtained by grafting. During impregnation there are no restrictions related to the available surface area or the silanol surface concentration and thus the whole porous structure can be impregnated with amines. Hence, higher organic loadings can be achieved, though it can also result in pore saturation.

Figure 5 shows FTIR spectra of impregnated-functionalized palygorskite. As explained above, some new bands corresponding to loaded polyethyleneimine (PEI) are detected, as well as those of the original palygorskite. In this case, all the bands previously detailed are now present, except those corresponding to methoxy groups, absent in the structure of PEI.



**Figure 7.** Nitrogen adsorption-desorption isotherms at 77 K of palygorskite-based samples Paly and Paly-PEI.

**Table 3.** Nitrogen content and CO<sub>2</sub> adsorption properties at 45 °C and 1 bar for PEI-impregnated clays.

Sample	mmol N/g ads	$q$ (mg CO <sub>2</sub> /g ads)	$q_m$ (mol CO <sub>2</sub> /mol N)
Bent-PEI	4.9	45.7	0.21
Mont-PEI	5.7	60.4	0.24
Paly-PEI	7.4	67.1	0.21
Sapo-PEI	6.7	66.9	0.23
Sepi-PEI	7.6	55.9	0.17

Pure CO<sub>2</sub> isotherms obtained for impregnated adsorbents are shown in Figure 8, with CO<sub>2</sub> adsorption data being listed in Table 3. CO<sub>2</sub> adsorption isotherms present features previously described as characteristic of chemical adsorption. In this case, these features are much more marked, as the amine loading is higher and so is the contribution of CO<sub>2</sub> chemisorption.

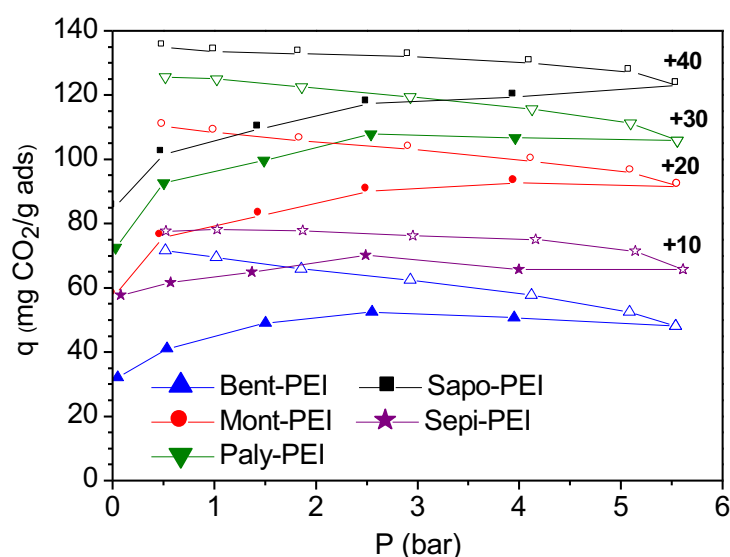
CO<sub>2</sub> uptake values at 1 bar ranged from 45.7 to 67.1 mg CO<sub>2</sub>/g ads, higher than the ones obtained by grafting. However, amine efficiency was between 0.17 and 0.24 mol CO<sub>2</sub>/mol N, with lower values than the ones registered for grafted adsorbents (0.23-0.49 mol CO<sub>2</sub>/mol N).

Lower amine efficiencies are commonly found for impregnated samples, especially when PEI is used. This is because the viscous nature of PEI hinders CO<sub>2</sub> diffusion and also its structure presents ca. 30 % tertiary amines, which do not react with CO<sub>2</sub> [63].

Comparing the different adsorbents, Sepi-PEI did not yield in this case the best results in terms of CO<sub>2</sub> uptake or amine efficiency. With a 30 % PEI occupying the inner porous structure and very likely clogging the smallest pores, it seems that the presence of micropores is not beneficial and other features are preferable for highly loaded samples.

Among the rest of the samples, Mont-PEI shows the best behavior in terms of amine efficiency (0.24 mol CO<sub>2</sub>/mol N), while having a high net CO<sub>2</sub> uptake (60.4 mg CO<sub>2</sub>/g ads) and the highest increase from the CO<sub>2</sub> uptake values of the raw clay mineral (10.1 mg CO<sub>2</sub>/g ads). This fact can be ascribed to the high surface area and pore volume of this material, which presents the highest values without taking sepiolite into account.

Due to the results obtained so far, both montmorillonite and sepiolite were selected as excellent candidates to perform further modifications by double functionalization techniques.



**Figure 8.** CO<sub>2</sub> adsorption-desorption isotherms at 45 °C of different functionalized clays obtained by impregnation with PEI.

### 3.4. Double functionalization of hydrated clays

Double functionalization was studied by impregnating PEI over montmorillonite and sepiolite previously grafted with AP or DT. In order to avoid saturation of the porous structure, the amount of PEI loaded was two and four-fold decreased compared to impregnated samples. Pure CO<sub>2</sub> isotherms for montmorillonite samples are presented in Figure 9 as an example and summarized data are listed in

Table 4.

Results obtained for these samples are summarized in Table 4. Nitrogen loadings ranged between 3.9 and 5.4 mmol N/g ads for montmorillonite and between 4.0 and 8.5 mmol N/g ads for sepiolite, being comparable or higher than those obtained by grafting or impregnating these clays independently (from 3.4 to 7.6 mmol N/g ads).

However, CO<sub>2</sub> uptake for double functionalized montmorillonite samples ranged from 6.0 to 17.7 mg CO<sub>2</sub>/g ads (see

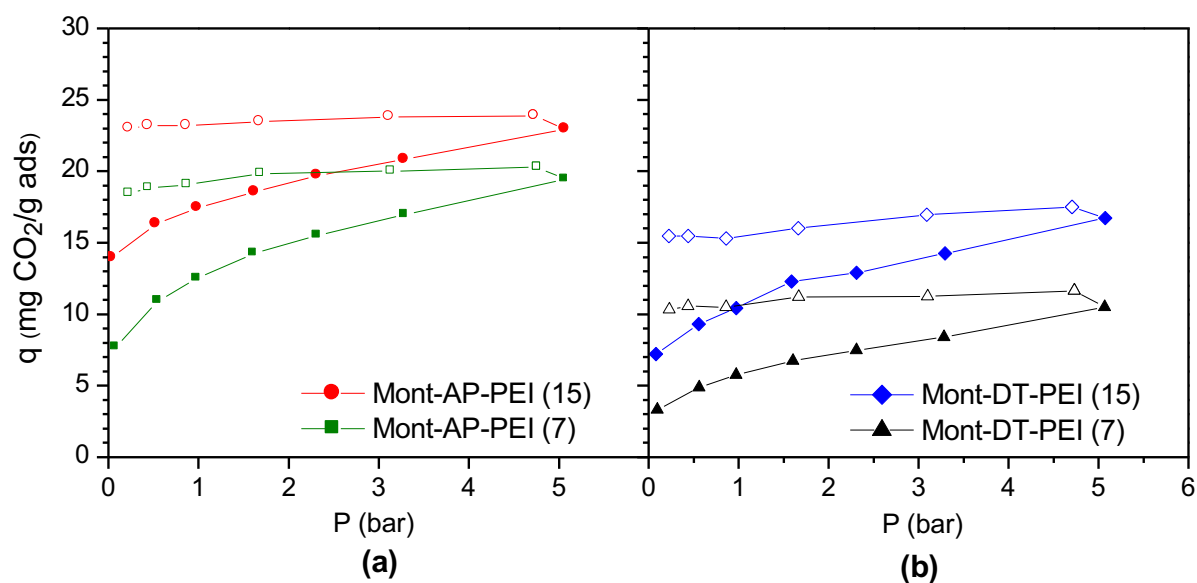
Table 4). These values are very far from those of grafted (33.1 and 50.0 mg CO<sub>2</sub>/g ads) or impregnated samples (60.4 mg CO<sub>2</sub>/g ads), being closer to that of non-functionalized montmorillonite (10.1 mg CO<sub>2</sub>/g ads).

In the case of sepiolite, CO<sub>2</sub> uptakes are in between 32.6 and 36.6 mg CO<sub>2</sub>/g ads. These values are lower than those achieved by independently modifying sepiolite wither by grafting (43.8 and 61.3 mg CO<sub>2</sub>/g ads) or impregnation (55.9 mg CO<sub>2</sub>/g ads) and also lower than the original unmodified material (40.7 mg CO<sub>2</sub>/g ads).

In addition, regardless the clay used both the net CO<sub>2</sub> uptake and the amine efficiency decreased when grafting the long-chained DT molecules instead of shorter AP. The increase in the amount of PEI yielded slight efficiency increases for montmorillonite but considerable drops in the case of sepiolite.

All the results described point to the fact that the porous structure of double functionalized samples could have been blocked after the double-functionalization treatment. This result is coherent with previous results by our group, since this novel technique resulted in noticeable CO<sub>2</sub> uptake and efficiency improvements when using supports with larger porous structures such as pore-expanded SBA-15 (D<sub>p</sub>: 15.2 nm; V<sub>p</sub>: 1.18 cm<sup>3</sup>/g) [45]. However, the use of an MCM-41-like support with equally large pore volume but much smaller pore diameter (D<sub>p</sub>: 5.1 nm; V<sub>p</sub>: 1.28 cm<sup>3</sup>/g) yielded more moderate increments [65]. In this case, the relatively restricted porous structure of montmorillonite and sepiolite in comparison with mesoporous silicas may be hindering PEI diffusion and thus giving rise to blocked pores. Even more, the grafting of long-chained DT molecules resulted in a more marked pore-blocking compared to the use of AP, as seen in the CO<sub>2</sub> uptake and amine efficiency results.





**Figure 9.** CO<sub>2</sub> adsorption-desorption isotherms at 45 °C of montmorillonite adsorbents obtained by double functionalization of montmorillonite: impregnation of PEI over AP and DT-grafted samples.

**Table 4.** Nitrogen content and CO<sub>2</sub> adsorption properties at 45 °C and 1 bar for double functionalized clays.

Sample	mmol N/g ads	q (mg CO <sub>2</sub> /g ads)	q <sub>m</sub> (mol CO <sub>2</sub> /mol N)
Sepi-AP-PEI (7)	4.0	36.6	0.29
Sepi-AP-PEI (15)	6.7	34.5	0.16
Sepi-DT-PEI (7)	7.0	34.8	0.16
Sepi-DT-PEI (15)	8.5	32.6	0.12
Mont-AP-PEI (7)	3.9	12.8	0.07
Mont-AP-PEI (15)	5.2	17.7	0.08
Mont-DT-PEI (7)	5.4	6.0	0.03
Mont-DT-PEI (15)	5.4	10.7	0.05

### 3.5. Influence of CO<sub>2</sub> dilution and water presence in clayey adsorbents

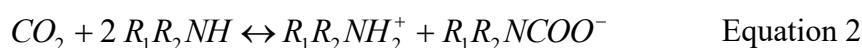
Finally, the behavior in simulated industrial post-combustion conditions was tested for three sepiolite materials, Sepi-AP, Sepi-DT, and Sepi-PEI, since overall this support yielded the best performance in CO<sub>2</sub> adsorption. A fixed bed coupled to a mass spectrometer was used, with

CO<sub>2</sub> partial pressure being of 0.15 bar, including the presence of moisture in the gas stream (ca. 5 %) and considering successive adsorption-desorption cycles. Sepiolite was selected for this study, since this clay achieved the best overall behavior towards CO<sub>2</sub> capture, including the highest CO<sub>2</sub> uptake in the series of AP and DT-grafted samples.

Figure 10 shows three adsorption-desorption cycles (numbered from 1 to 3) under the above-described conditions. Additionally, CO<sub>2</sub> uptake at 0.15 bar CO<sub>2</sub> in dry conditions was obtained from adsorption isotherms in each case and included in Figure 8 as initial value.

Firstly, the influence of 5 % water was found to be advantageous for all the adsorbents. AP and DT grafted samples underwent an increase of 23 and 17 % respectively compared to dry CO<sub>2</sub> adsorption.

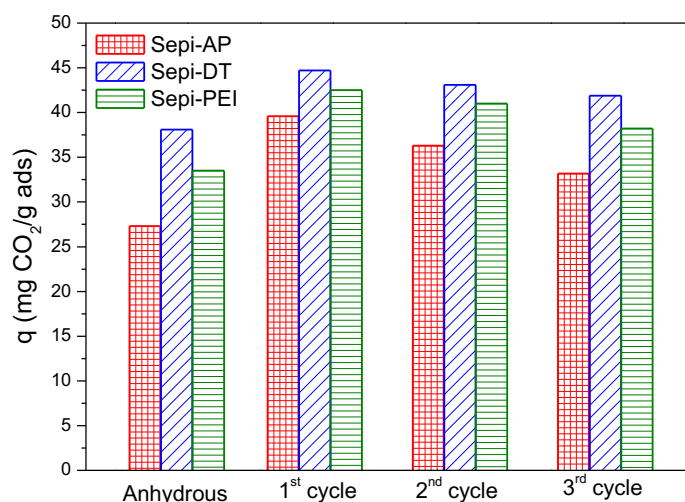
This increase can be explained by the different chemical reactions between CO<sub>2</sub> and amines in anhydrous or wet conditions. Under anhydrous conditions, CO<sub>2</sub> reacts with primary and secondary amines (Equations 1 and 2, respectively) following a 1:2 stoichiometry. On the contrary, a different reaction takes place in the presence of moisture (Equation 3), having a 1:1 stoichiometry [10]. Since this value doubles the 1:2 ratio observed in anhydrous conditions, this could lead to a theoretical increment of 100 % in the CO<sub>2</sub> uptake.



In the practice, reported increments for DT-grafted samples are usually much lower, such as 10 % [66,67], 6 % [68], 3 % [69] or even negative values [61], which is coherent with the 17 % increment observed here for DT-modified sepiolite.

The adsorbent impregnated with PEI underwent a 27 % increase when changing from dry conditions to 5 % moisture. This rise is the highest in this series and is in line with increments of 24 % [70] and 55 % [69] reported for similarly PEI-impregnated materials.

Successive adsorption-desorption cycles showed that all the samples experienced a certain decrease in their CO<sub>2</sub> uptake after the third cycle. However, the adsorption uptake that still remained is considerable in all cases: 83.8 % for AP, 93.7 % for DT and 89.2 % for PEI. These values are coherent with those reported in the literature, where grafted samples maintained 93% of their initial CO<sub>2</sub> uptake after 100 cycles [71].



**Figure 10.** Pure CO<sub>2</sub> uptake of amine-containing sepiolite adsorbents under anhydrous (one cycle) and wet conditions (three cycles).

## Conclusions

A series of clay materials were modified by grafting with aminopropyl (AP) and diethylenetriamine (DT) trimethoxysilanes and by impregnation with polyethyleneimine (PEI). Double functionalization technique was also applied by impregnating the previously grafted samples.

Among the series of clays modified by grafting, AP-containing materials were generally found to incorporate higher silane loadings than DT-samples due to steric hindrances in the latter. Nevertheless, most DT-grafted clays contained a higher amount of nitrogen than their AP counterparts due to the higher amino content in DT molecules compared to AP. A similar behavior was observed for CO<sub>2</sub> uptake, where Sepi-DT yielded a maximum value of

61.3 mg CO<sub>2</sub>/g ads. In general, grafted adsorbents showed high efficiency, with molar CO<sub>2</sub>/N ratios being of 0.23-0.49 mol CO<sub>2</sub>/mol N.

PEI-impregnation and double-functionalization yielded higher organic loadings but lower amine efficiencies than grafted samples, both originated by the higher density of amines in polyethyleneimine. PEI-impregnated materials yielded good CO<sub>2</sub> adsorption properties, with net uptakes up to 67.1 mg CO<sub>2</sub>/g ads and amine efficiencies as high as 0.21 mol CO<sub>2</sub>/mol N. However, double-functionalized samples suffered pore-blocking due to the high organic loading and showed CO<sub>2</sub> adsorption capacities lower than those achieved by individual grafting or impregnation.

These results show that the five studied clays are able to produce interesting and low-cost CO<sub>2</sub> adsorbents provided that the organic amount loaded is not too high.

When moisture was present, the amount of CO<sub>2</sub> adsorbed onto these materials was higher (17 to 27 % of increment) compared to dry uptakes due to the change in the CO<sub>2</sub>-NH reaction stoichiometry.

After three adsorption-desorption cycles, AP and DT-grafted adsorbents were found to be more stable than PEI-containing sample, which underwent a slight decrease.

As a result, clay-based materials have been proved to be inexpensive and good CO<sub>2</sub> adsorbents, useful to industrial purposes where moisture is present.

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