Preparation and morphological and physicochemical characterization of pillared clays from bentonite

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Abstract. Mineral grade and commercial grade bentonite pillared clays were prepared with SnO₂. This is to create adsorbents for removal of contaminants from water. The initial and modified clays were characterized by X-ray fluorescence (XRF), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and nitrogen sortometry. The results of the chemical analysis (XRF) clearly confirm the incorporation of tin in the modified materials. The analysis by SEM and nitrogen sortometry verified the successful modification of the clays by incorporation of tin dioxide species, and the appearance of mesoporous structures with an increase in the values of surface area and porosity.

1. Introduction
In recent years, the so-called emerging pollutants (or micropollutants) have attracted considerable interest. They are compounds of diverse origin and chemical nature, whose presence and consequences in the environment have gone unnoticed. They are present in water in low concentrations of ngL⁻¹ to μgL⁻¹ and are considered very harmful to human health and the environment. They can cause various effects in organisms, such as chronic toxicity, endocrine disruption and bioaccumulation [1].

One of the main problems of this type of pollutant is that current wastewater treatment plants are unable to eliminate them. These are designed to remove organic matter and nutrients in higher concentrations (gL⁻¹). Therefore, emerging pollutants are present in surface waters, groundwater and for human consumption [2].

The methods used to treat emerging pollutants can be classified into three families: physical-chemical treatments, biological treatments, hybrid processes and advanced oxidation processes (AOPs). One of the most studied physical-chemical treatments for water treatment are adsorption processes, especially for the elimination of organic pollutants. That is why they have also been widely studied for their application in the elimination of emerging pollutants [8].

The most commonly used adsorbents are activated carbons: granular activated carbon (GAC) or powdered activated carbon (PAC). their main advantage is that they do not generate toxic products and have a high adsorption capacity [3-8]. The adsorption efficiency is a function of the properties of the adsorbent used, such as surface area, morphology and surface chemistry [4].

There are also other studies using other types of adsorbents, such as zeolites, clays or carbon nanotubes. Among the clay minerals, there are smectites or montmorillonites, which are characterized by having a moderate interlaminar load with good expansion capacity, which allows them to "swell"
when they are introduced in an aqueous medium and to be chemically modified by intercalation-pillerization with bulky molecular species [5].

Pillarization consists of introducing, in the interlaminar space of a smectite, a very voluminous polycation that, after calcination, gives rise to a stable oxide that determines a fixed and permanent porosity of controlled size (molecular sieves). The fields of application of these materials (pillared clays) are very wide due to the possibility of intercalating different types of pillars, making them suitable for specific adsorption, molecular separation, or heterogeneous catalysis processes in a wide range of reactions [6].

Due to the above, it is very important to find alternative solutions for the degradation of emerging pollutants present in bodies of water. The objective of this work is to obtain from the preparation of new materials such as pillared clays, to use them in the degradation of emerging pollutants.

2. Materials and methods

2.1. Materials

The mineral bentonite (Bt) used in this study was supplied by Mining and Commercial Projects of Colombia S A S (Puerto Colombia, Atlántico) and the commercial Na-K-Bentonite was acquired from Sigma-Aldrich. Mineral bentonite and commercial bentonite were pretreated with a Na₂CO₃ solution (0.5M) for 24h and washed thoroughly with copious amounts of deionized water. The pillarizing agent was prepared by the dropwise addition of 50 mL chloride of tin (II), SnCl₂·2H₂O (0.4M) to 50 mL of KOH (0.4M) with continuous stirring at 70 °C for 24h. 5.0g of Bt were mixed with 400 mL of deionized water and then 100 mL of the pillarizing agent was added to the clay suspension, with continuous stirring at 60 °C for 24 hours. The result of the suspension was washed with abundant deionized water by means of centrifugation around 6 replicates. The collected material was dried at 80 °C for 24h and calcined at 500 °C for 3h. This process was performed for both mineral grade bentonite and commercial grade bentonite.

2.2. Methods

Nitrogen isotherms were measured at -196 °C using a Gemini 2375 instrument (Micromeritics). Before each measurement the samples were degassed under vacuum at 160 °C for 4h. The surface area (BET) was calculated from the isotherms. Spectroscopy (FT-IR) was performed in the Nicolet iS10 spectrophotometer, by means of the preparation method of pellet. The KBr pellet with the sample was subjected to heating at 100 °C for 1h.

Scanning electron microscopy (SEM) was performed in an FEI microscope (ESEM) Quanta 200, with a resolution of 10 µm at 25 kV. The analyzes were carried out with the samples previously subjected to heating at 100 °C for 1h. A thin layer of gold was coated, as it was a poorly conductive sample. The elemental chemical analysis was carried out on an X-ray fluorescence spectrometer, MagixPro PW-2440 Philips (WDXRF) equipped with a Rhodium tube, with a maximum power of 4KW. The semi-quantitative analysis was carried out with the SemiQ 5 software, making 11 scanning, in order to detect all the elements present in the sample.

3. Results and discussion

3.1. Samples’ characterization

The changes in porosity when pillared are reflected in nitrogen absorption, see Figure 1 and 2. The isotherms present higher nitrogen adsorption volumes in the pillared bentonites than in the starting bentonites, highlighting the increase in the porosity of bentonites as a consequence of tin modification. The shape of all isotherms allows them to be classified as type II, according to the IUPAC classification [7]. This is typical of solids with macro and mesopores. Furthermore, the desorption branch of the isotherms forms hysteresis type H3, which is attributed to pores in the form of slits with non-uniform sizes [7, 9, 10].
The parameters of the porous structure calculated with the StarDriver V2.03 software are shown in Table 1. As can be seen, the surface area and the volume of the micropore increased almost two times after pillarization. The increase in surface area and porosity must be attributed not only to the pillarization process, but also to the deposition of tin oxide on the outer surface of the bentonite flakes and the aggregation of these flakes. The micropore volume value of unpillared commercial bentonite is due to the drying process that typically adds soda ash (anhydrous sodium carbonate). This serves to improve the expansion properties of bentonite, which is then processed through coal or gas rotary dryers, to which, if too much heat is applied, many of the properties of bentonite can be destroyed; in this case, the micropore volume was affected by this process.

### Table 1. Comparison of the textural properties of mineral and commercial bentonite.

|        | BET surface area (m²/g⁻¹) | Micropore area (m²/g⁻¹) | External surface area (m²/g⁻¹) | Pore size (nm) | Micropore volume (cm³/g⁻¹) |
|--------|---------------------------|-------------------------|-------------------------------|---------------|--------------------------|
| Bt-min | 44                        | 13                      | 31                            | 4.20          | 0.005                    |
|        | not pillared              |                         |                               |               |                          |
| Bt-min | 131                       | 21                      | 109                           | 3.30          | 0.010                    |
|        | pillared                  |                         |                               |               |                          |
| Bt-com | 4                         | 0.62                    | 4                             | 24.02         | 0.000                    |
|        | not pillared              |                         |                               |               |                          |
| Bt-com | 70                        | 16                      | 53                            | 4.99          | 0.007                    |
|        | pillared                  |                         |                               |               |                          |

The spectra (FT-IR) are shown in Figure 3, where you can see the characteristic bands at 3620 cm⁻¹, this correspond to stretching vibrations of structural OH groups of aluminum in octahedral coordination; the bands observed at 1635 cm⁻¹ are the deformations of the O-H bond of the adsorbed water and the bands observed at 1019 and 980 cm⁻¹ correspond to stretching vibrations of Si-O in the structure of the clay mineral [9, 10]. It can be seen that there are small displacements in the bands at the time of pillarizing the clays, this is due to the stretching vibrations of Sn-O observed at 548 and 552 cm⁻¹, which gives us indications that there was a modification in the clay mineral structure.
The SEM micrographs of the starting mineral bentonite and the pillared mineral bentonite are shown in Figures 4 and 5. These images reveal the variations in morphologies. The surface of the starting bentonite is smooth with respect to the pillared bentonite, which shows a less smooth surface, this is due to the formation of grains with highly eroded surfaces and can be associated with the delamination of the mineral [9,10].

**Figure 3.** Infrared spectra of mineral bentonite and commercial bentonite.

**Figure 4.** Micrograph of mineral bentonite without pillars.

**Figure 5.** Micrograph of mineral bentonite pillared.
X-ray fluorescence analysis was performed to identify and quantify the elements that were present in both the starting bentonite and the pillared bentonite. Table 2 shows the starting bentonite that has a high content of silicon (52.44%) and aluminum (20.01%), this being the typical composition of a montmorillonite, in this case bentonite. A high content of sodium (10.86%) can also be seen, which is characteristic of sodium bentonites. From the analysis of the pillared bentonite, table 2 shows an increase in potassium (1.01%) and a notable decrease in sodium (0.46%) with respect to the starting bentonite. This is due to the cation exchange that took place. A high content of tin (28.79%) is also seen, evidencing the effective incorporation of SnO$_2$ species in the pillarization process. In addition, table 2 shows a slight decrease in silicon (41.1%) and aluminum (13.91%) and this is attributed to the incorporation of the pillar.

Table 2. Chemical analysis of the starting bentonite and the pillared bentonite.

| Elemento y/o Compuesto | Bt-min without pillars (%) | Bt-min pillared (%) |
|------------------------|-----------------------------|---------------------|
| Sn                     | -                           | 28,79               |
| Si                     | 52,44                       | 41,1                |
| Al                     | 20,01                       | 13,91               |
| Na                     | 10,86                       | 0,46                |
| Fe                     | 8,25                        | 10,35               |
| Mg                     | 5,90                        | 1,13                |
| Ca                     | 1,80                        | 0,92                |
| K                      | 0,74                        | 1,01                |
| Ti                     | -                           | 1,45                |
| Cl                     | -                           | 0,14                |

4. Conclusions
According to the results obtained in this work, it is concluded that the bentonites modified by the incorporation of tin oxide through the pillarization process showed an improvement in the textural parameters, increasing the volume of the micropores, the surface area and generating controlled porosity in solids. This indicates that the SnO$_2$ particles not only intercalated within the space of the interlayer of clay, but also precipitated on the outer surface of the clay flakes.

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