

## Synthesis and characterization of Sb-PILCs Bentonite Clay Mineral used as Adsorbent

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### ABSTRACT

**Abstract:** The Objective of our study is the valorization of clay of the western region of Algeria. The experimental study is the preparation and characterization of Antimony pillared materials using  $SbCl_3$  solution as pillaring agent. The synthesis of pillared clay was characterized by different techniques namely (FTIR, XRD and XRF) and physic-chemical analyzes (CEC, the acid index, specific surface area, average pore diameter, and volume mass). The intensity of the Bands assigned to Si-O and Al-O Vibrations were slightly reduced on pillaring process. The decrease in intensity is due to the process of dehydroxylation produced during pillaring. The d-spacing for the intercalated and pillared bentonites is  $38.199 \text{ \AA}$  and  $30.057 \text{ \AA}$ , respectively. The specific surface area of pillared and natural bentonite is  $365.11$  and  $68.25 \text{ m}^2 \text{ g}^{-1}$  respectively. With determined specific properties, modified clays are highly reactive matrices that can be used as adsorbents in the process of depollution of industrial wastewater.

### I. Introduction

The porous solids in general and in particular clays, are characterized by their ability to adsorb metals, and organic substances contained in aqueous solutions [1]. However, its importance is subject to the influence of several parameters: temperature, pH, nature of the adsorbed element [2]. The natural physical and chemical properties of the clays as cation exchange capacity, high specific surface area, porosity and surface acidity are strongly related to their atomic structure, inter-crystalline texture and chemical composition [3]. It often makes changes to these properties in order to obtain a very special adaptation for a job well defined treated clays. The substitution of the exchangeable cations, the insertion of organic and inorganic molecules and activation acid practice more and more on clay materials [4]. Activated clays are generally used for the preparation of bleaching earth, adsorbents in the clearance processes of industrial wastewater and acid catalysts. [5].

To expand the scope of clays traps pollutants as metals, it has become necessary to address the issue of the closure of their slips, speaking to  $200^\circ \text{C}$ . This disadvantage was overcome by pillaring: Intercalation of cationic complexes of large size, which by calcinations, would turn into pillars of oxides, helped maintain their open structure and create micropores in the interlayer space, thus improving their adsorptive properties [6].

The intercalation is effected by the exchange of interlayer cations ( $Na^+$ ,  $Ca^{2+}$ ) or by other hydroxypolymers polycations such as  $Al_{13}$ , a controlled higher calcination stabilizes by dehydroxylation pillars giving rise to a rigid structure which has better mechanical properties and the possibility of being reusable. The possibility of incorporating multivalent cations or bulky allows clays to increase their surface acidity or porosity and thereby become acidic molecular sieves with large pores as an alternative to activated carbon [7, 8]. The polycation ultradispersion of aluminum, antimony and iron in the material may provide Clays better retain pollutants divalent metal

cations such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ .... . Indeed, large specific surface areas of these materials would develop surface groups acting as ligands in higher concentration, allowing a more consistent chemisorption of divalent cations existing in the waters of industrial discharges [9]. The pillared structure has been suggested to produce acid sites through dehydration and dehydroxylation of the metal cations at high temperature; the number and strength of the acid sites present in the clay are important factors for exchange and adsorption applications. The pillaring clays contain total surface acidity that varies with the pillaring agent and can be studied by IR spectroscopy using pyridine or n-buthylamine adsorption-desorption process [10].

Considering the importance of the phenomenon of activation followed by pillaring operation in the clay applications. We study in this work, synthesis and characterization of modified clay materials used as adsorbents.

## II. Materials and methods

### II.1. Preliminary treatment

All experiments in this work were performed on the batch of rich smectite (montmorillonite) deposit from Maghnia west of Algeria. The crude clay is crushed and sieved to a particle size less than 20 microns. This screening operation can significantly reduce the amount of impurities (quartz, feldspar...) by removing large particles corresponding; therefore facilitating the subsequent operations of treatment. Bentonite underwent the first treatment solution ( $\text{Na}_2\text{CO}_3$ , Fluka) in 1.5 M with the aim of having a homological sodic clay, the second treatment solution ( $\text{H}_2\text{SO}_4$  96%, Aldrich), concentration 3 mol/L at temperature 70 °C, in proportions of 10 g of clay per 300 ml solution for 4 hours .The mixture clay/acid is then separated by centrifugation. The solid phase is washed twice with hot distilled water to remove excess sulfuric impregnating its external surface, dried in an oven for 48 hours at 110°C, crushed and then stored away from moisture.

### II.2. Preparation of Sb-pillared clay synthesis

The polycation solution of Antimony is prepared by the polymerization reaction of the  $\text{Sb}^{3+}$  ion is performed according to the operating conditions shown in **table 1**. In this synthesis, we proceed to the titration of a solution of 0.4 M antimony chloride ( $\text{SbCl}_3$ , Prolabo) with a basic solution to 0.72 M ( $\text{NaOH}$ , Fluka). Titration is carried out by means of a funnel drips. When titrating, the homogenization of each solution is performed by a mechanical stirrer fitted with a metal rod to prevent formation of the metal hydroxide precipitate. We followed daily monitoring of pH and color of the pillaring solution according aging time. Thereafter,

the pillaring solution was added drop wise to about 10 g of the activated clay in 50 ml suspension, for one hour homogenized well are titrated by drop wise pillared solutions of antimony in agitation (500 rpm / min) until mechanical homogenization. The mixture was then dialyzed for 4 days against distilled water once a day is renewed. Drying is performed at 110 ° C; the powder was calcined at 500 ° C, for 3 hours in a muffle furnace. The resulting product is Antimony Pillared clay Mineral (Sb-PILCs).

**Table 1.** Characteristics of Sb-pillared solution.

<b>Sb-pillaring solution</b>	The Antimony polycation
<b>Formula polycation</b>	No identifying
<b>Symbol</b>	$\text{Sbx}(\text{OH})_y$
<b>Molar ratio</b>	$\text{OH}/\text{Sb} = 2.2$
<b>Aging time (hours)</b>	80 h

### II.3. Characterization of Sb-Pillared and natural clay Sample:

The Chemical composition of the clay samples were analyzed using by X-Ray fluorescence spectrometry (Princeton Game Technology).The structural modifications of the clay samples were identified by Infrared-Spectroscopy: IR spectra were recorded between 4000  $\text{Cm}^{-1}$  and 400  $\text{Cm}^{-1}$  using an IR-FT spectrometer Nercolet 560 coupled to a digital computer. The samples are formed into self-consistent in KBr pellet (1%).Powder X-Ray Diffraction patterns were recorded on an automatic diffract meter anticathode excited copper under voltage 40 KV, Philips brand, the sample is prepared according to the method of pasta oriented in the clay phase. The Physic-chemical properties of the raw and modified clay were determined by the following techniques: The cation exchange capacity by the adsorption of ethylene diamine complex. The total surface acidity by the adsorption of a solution of n-buthylamine taking excess reacts and the rest of the solution is titrated back with  $\text{HClO}_4$ .The Specific Surface area ( $S_{\text{BET}}$ ) and Average pore Diameter by the BET method. Volume Mass ( $\rho$ ) by the pycnometer method. For the determination of copper, the apparatus used is an atomic absorption spectrophotometer double beam Perkin Elmer 1100B brand category. The pH measurement is made with a digital pH meter pH 212 HANNA laboratory equipped with a combined electrode.

## III. Results and discussion

### III.1. Chemical Composition of the clay samples

The chemical composition of both pillared and unpillared bentonite clay is shown in table 2. The results indicate that the natural bentonite contains silica, alumina, magnesia, iron (III) and sodium oxides as major constituents while traces of calcium and potassium oxides. Depending on the overall composition of the natural clay sample, it is a montmorillonite [4]. The value of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio being about 2.72 characterizes montmorillonite, according to some authors, when it varies between 2 and 5.5 [4]. From the results in table.1, analysis by X-ray fluorescence showed the presence of antimony (its value is 19.60% in the processed state) after the pillaring operation that confirm the presence of antimony pillars in the interlayer space of the clay mineral. On pillaring, the Antimony content increased while other metals decreased significantly due to ion exchange and washing several times with water.

**Table 2.** The chemical composition of unpillared and Sb-pillared bentonite clay minerals (Weight %).

Chemical Composition	Unpillared Bentonite (%)	Sb-pillared Bentonite (Calcined at 500°C) (%)
SiO <sub>2</sub>	61.10	61.20
Al <sub>2</sub> O <sub>3</sub>	22.10	16.01
Fe <sub>2</sub> O <sub>3</sub>	7.84	2.10
MgO	4.04	1.04
CaO	1.00	0.01
Na <sub>2</sub> O	2.15	0.02
K <sub>2</sub> O	0.28	0.01
TiO <sub>2</sub>	0.05	-
SO <sub>3</sub>	0.01	-
As	-	-
Sb	-	19.60
Loss on ignition	1.43	0.01
<b>Total</b>	<b>100</b>	<b>100</b>

### III.2. Determination of cation exchange capacity (C.E.C) and total Surface acidity of the clay materials samples

This measurement of the cation exchange capacity shown in table.3, is an indication primordial of the number of available cation exchange. The results of the CEC for the raw bentonite is in agreement with literature data, because the latter following the CEC of the unpillared clay not exchanged between 70 meq/100g and 150meq/100g according to some authors. [1.2].

For pillared sample of bentonite : we see a good CEC this is due to the presence of the pillars (the intercalation of polymeric species of antimony in the interlayer volume) have spaced as possible the layers of clay mineral that facilitates the exchange transaction to take place. These results are consistent with the literature data [1.3].

Species that we call "**pillars**" generate certain acidity by a contribution of protons. Generally, the **total surface acidity** increases with the degree of pillaring of metal hydroxyl-pillars according to some authors.

**Table 3.** Results of the CEC and Total surface acidity of unpillared and Sb-pillared bentonite clay minerals.

Samples	C.E.C [meq /100g]	Surface acidity [meq/g]
Unpillared bentonite	86	1.05
Sb-pillared bentonite (Calcined at 500 °C)	131	1.85

### III.3. Specific Surface area-pore diameter, volume Mass measurements of the clay samples

Analysis of physical properties of the raw and modified clay materials are shown in table 4, showing an improvement in the porosity of the intercalated and pillared material compared with the raw material, which shows an increase in the interlamellar spaces and improving of the porous texture of the materials studied. The calcination at 500 °C of the intercalated clay actually increases the specific surface area following the destruction of

Organic matter, According to some authors. [1.3]. The pore diameter and the volume mass of the intercalated and pillared bentonite are significantly higher than that of the unpillared sample due to the presence of the microporous texture created by the antimony pillars in the interlayer regions.

The average pore diameter is within the range typical of smectite clays. Similar observations were reported by Bacar and Nistor for the effect of the **preparation** parameters on the structural and textural properties of intercalated clays iron (III) [1.2.].

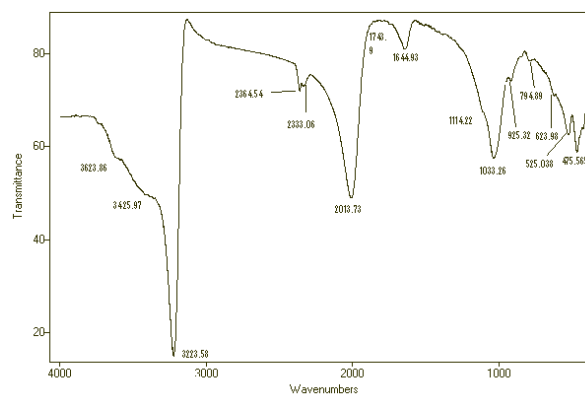
**Table 4.** Results of Specific Surface area-pore diameter, Volume mass of un-pillared and Sb-pillared bentonite clay minerals.

Samples	Natural bentonite	Intercalated bentonite	Sb-pillared bentonite (calcined at 500°C)
Specific Surface Area ( $S_{BET}$ , $m^2/g$ )	68.25	250.10	365.11
Pore Diameter (Dm, $\text{Å}$ )	47.6	58.4	98.8
Volume Mass ( $\rho$ , $g/cm^3$ )	2.34	2.62	3.93
The interlayer Space ( $\text{Å}$ )	14.47	38.199	30.057

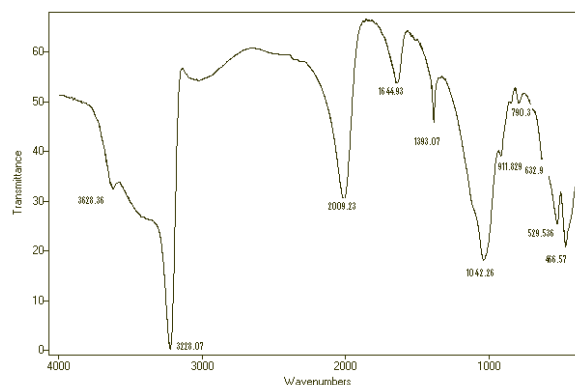
### III.4. Infrared Spectroscopy

Infrared Spectroscopy is a very important way for investigating structural changes in pillared clay frameworks. The region of interest for determining structural composition is the frequency region between  $1400-400\text{ cm}^{-1}$  which is characteristic of metal bonded silica. The FTIR spectra of the natural bentonite and antimony pillared bentonite are shown in **Fig.1** and **Fig.2**. Infrared spectroscopy applied to clay materials, helps differentiate between molecules of water of hydration and hydroxyl constitution and follow the structural changes in the modification in Pillaring [6, 7]. The IR Spectrum of the natural bentonite (**Fig.1**) shows an intense peak at around  $1400\text{ cm}^{-1}$  that is due to bending vibrations of water. The spectra show two absorption bands between  $3000-3800\text{ cm}^{-1}$  and between  $1600-1750\text{ cm}^{-1}$ . The bands that stretch entre  $1600-1750\text{ cm}^{-1}$  are attributed to stretching vibrations of the **OH group** of the water content more vibration binding adsorbed water. The band in the range  $3000-3800\text{ cm}^{-1}$ , with a strong peak at the shoulders  $3625$  and  $3200-3450\text{ cm}^{-1}$  characterizing montmorillonite corresponds to the stretching vibrations of the OH groups of the octahedral layer at coordinates  $1Al + 1Mg$  ( $3640-3623\text{ cm}^{-1}$ ) or  $2Al$  ( $3623\text{ cm}^{-1}$ ). The **Si-O** bonds are characterized by the following absorption bands: -The intense band between  $900-1200$  is centered around  $1033\text{ cm}^{-1}$  and  $1037\text{ cm}^{-1}$  corresponds to the stretching vibrations of **Si-O bond**. The bands located at  $525.038$ ,  $525.04$  and  $466.57$ ,  $475.565$ ,  $471.067\text{ cm}^{-1}$  are assigned respectively to deformation vibrations of **SiOAl<sup>VI</sup>**, **SiOMg<sup>VI</sup> bonds**, **Si-O-Fe. Liaison Me<sup>VI</sup>-OH** (**Me=Al, Mg and Fe**). The strips of Al-OH vibrations are observed between  $910$  and  $916-923\text{ cm}^{-1}$  for modified bentonites. Sharing the OH group of atoms Fe and Al in octahedral position can move Al-OH vibrations to lower frequencies around  $790.30$ ,  $794.89\text{ cm}^{-1}$  and  $916-923$ ,  $925.32\text{ cm}^{-1}$ . Thus, vibration Mg-O and Mg-OH (Merged with

the **SiO**) are located at  $629.98\text{ cm}^{-1}$ . The intensity of the Bands assigned to Si-O and Al-O Vibrations were slightly reduced on pillaring process. The decrease in intensity is due to the process of dehydroxylation produced during pillaring.



**Figure 1.** FTIR spectra of un-pillared (Natural) bentonite.



**Figure 2.** FTIR spectra of Sb-pillared bentonite (calcined at  $500^\circ\text{C}$ ).

### III.5. Results of X-ray diffractograms of the modified Clays

The XRD patterns of the Sb-Intercalated and Sb-pillared bentonites are shown in **Fig.3** and **Fig.4**. The mineralogical study of these modified clays shows that these materials are mainly composed of montmorillonite (smectite) which is manifested by the appearance of peak at  $15.5\text{ Å}$  and, Cristobalite by the appearance of a peak at  $2.23\text{ Å}$  and the appearance of a peak of Quartz at  $3.33\text{ Å}$  and  $4.02\text{ Å}$  (001 reflection). The diffractogram of the intercalated and pillared clay materials shows an increase of the basal area due to the inclusion or intercalation of polymeric species (the pillars of antimony in the interlayer space) have spaced as possible the layers of clay mineral. The d-spacing for Antimony-intercalated and Sb-pillared bentonite is  $38.199\text{ Å}$  and  $30.057\text{ Å}$ , respectively, are shown in table.4 and.5. The basal spacing obtained for the sheets of the intercalated

and pillared clay materials confirm the great development of the micro porous network and large specific surface area. We can therefore conclude. That there is an improvement of the porous texture (a rigid microporous structure). Calcinations thus causes the loss of hydroxyl antimony's interposed [1, 2].

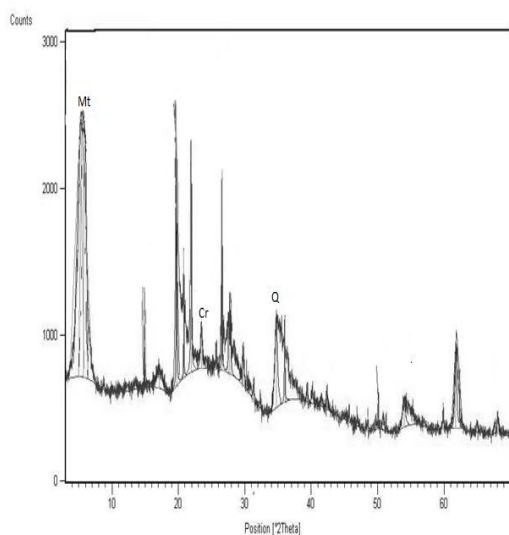


Figure 3. XRD pattern of Sb-Intercalated bentonite sample (Mt: montmorillonite, Q: Quartz, Cr: Cristobalite)

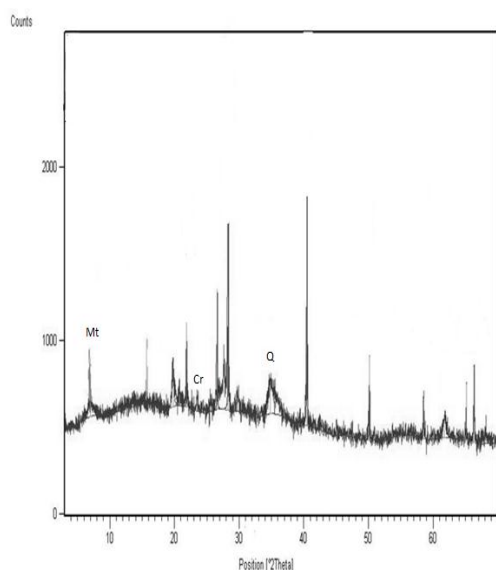


Figure 4. XRD pattern of Sb- pillared bentonite sample (Mt: montmorillonite, Q: Quartz, Cr: Cristobalite).

Table 5. D-Spacing for Intercalated bentonite and Sb-pillared bentonite.

Natural bentonite		Intercalated bentonite		Sb-pillared bentonite		mineralogical analysis
2 $\theta$ (°)	d <sub>001</sub> (Å°)	2 $\theta$ (°)	d <sub>001</sub> (Å°)	2 $\theta$ (°)	d <sub>001</sub> (Å°)	
7.6	4.71	7.4	38.199	7.4	30.057	Montmorillonite
36.55	1.87	36.55	4.02	36.55	3.33	Quartz
21.80	2.23	21.80	2.23	21.80	2.23	Cristobalite

#### IV. Conclusion

The characterization results of this study show that the Sb- intercalated and Sb-pillared bentonites have a high thermal stabilities and surface areas. The analyzed by infrared spectroscopy confirmed the existence of structural changes highlighted by the clay pillaring process and can be obtained under certain optimal conditions of preparation. We managed to prepare modified clay materials with basal spacing ranging from of 30.057 Å° to 38.199 Å° depending on the nature of the intercalated polycation complex. The textural analysis by the XRD and BET method of the Sb-Pillared and intercalated bentonite allowed us to confirm the creation of a dense micro porous network compared to the natural clay, caused by the intercalation of large metal pillars. With the properties determined, Sb-Pillared and intercalated bentonites clay are highly reactive matrices which can be used in decontamination processes of industrial wastewater.

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