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ORIGINAL RESEARCH PAPER

INFLUENCE OF SYNTHESIS PARAMETERS ON MORPHOLOGICAL PROPERTIES OF ALUMINUM(III)-PILLARED BENTONITES

Ana-Maria Georgescu[1*], Françoise Nardou[2], Ileana Denisa Nistor[1]

[1]"Vasile Alecsandri" University of Bacău, Faculty of Engineering, Chemical and Food Engineering Department, 157 Calea Mărăşeşti Street, 600115 Bacău, Romania
[2]University of Limoges / CEC, SPCTS, UMR 7315 CNRS, 12 Rue Atlantis, 87068 Limoges Cedex, France

*Corresponding author: ana.georgescu@ub.ro

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Abstract: Al-pillared interlayered clays (Al-PILCs) have been prepared from Romanian natural calcium bentonite (Orasu Nou deposit) and the effect of some parameters on the morphological properties has been investigated. The synthesis of Al-pillared bentonite consists in the following five steps: bentonite purification, ionic exchange of bentonite with Cu(II) ions, preparation of pillaring agent, intercalation of ionic exchanged bentonite with pillaring agent and calcination. The pillared clays present a rigid structure, a high thermal stability given by the oxido-metallic pillars formed after calcination. The raw material and the obtained nanomaterials were characterized by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). The intercalation of the Al-polyhydroxocations into the interlayer of montmorillonite strongly modified the morphology of the Al-PILCs. The material with the best characteristics will be chosen in the aim of its using in liquid effluents remediation.

Keywords: *Al(III)-pillaring, calcination, calcium bentonite, SEM-EDX, TEM*

INTRODUCTION

The interest shown in recent years in research studies of clay minerals is justified by their special properties and by their abundance in nature. At global level, the clays are used in many fields, the natural materials being chemically, thermally, mechanically or combined modified. Thus, clay materials can be successfully obtained in areas such as: environmental remediation (adsorbents or ion exchange), food industry, medicine, pharmacy, manufacture of pigments for paints, manufacturing paper, insecticides etc.
Montmorillonite belongs to smectite clay mineral group, with a double-layered structure (2:1), it being the most used type of clay in pillaring process. The synthesis of different metal oxide pillared interlayered clays (PILCs) led to the obtaining of microporous materials with special properties. There are many elements which have the ability to act as pillaring agents: Al, Fe, Cr, Ti, Mn, Cu, Zr, Ni etc. [1 – 6]. Aluminum is the first and the most intensive studied from these elements.
Pillared clay has to accomplish the following three criteria: chemical and thermal stability; existence of a sequence of layers that allows the determination of the basal distance (d_{001}); accessibility into interlamellar space of the molecules at least as large as nitrogen [3].
The conventional method of pillaring clays comprises two successive steps: the intercalation of the pillaring agent followed by the mineral calcination. The first step is done by slowly addition of a dilute solution of pillaring agent into a dilute dispersion of mineral clay. The properties of the intercalated mineral clay depend on many factors as: the nature and particle size of mineral clay, the nature of the polyhydroxocation, hydrolysis conditions (*p*H, OH / cation molar ratio, temperature), the duration and temperature of pillaring agent aging, the type of washing of the intercalated mineral clay (filtration, centrifugation and / or dialysis), temperature and drying conditions of the intercalated mineral clay (room temperature, in the oven at a low temperature, freeze drying) [3 – 6].
Our study presented in this paper consists in preparation of Al-pillared interlayered clays, using a Romanian natural calcium bentonite from Oraşu Nou deposit as raw material. Some synthesis parameters were varied in order to obtain advanced materials which will present adsorption properties.
The aim of this paper consists in the observation of evolution for morphological and chemical modifications that can occur after Al(III)-pillaring process of Romanian calcium bentonite, for chosen the adsorbent that presents the best properties for its using in heavy metals adsorption from liquid effluents.

EXPERIMENTAL CONDITIONS

Materials

A Romanian natural calcium bentonite (*CaBent-nat*) from Oraşu Nou deposit was used as raw material. The mineralogical composition and the characteristics of raw material, which were provided by the manufacturer (S.C. Bentonita S.A.), were presented in a previous paper [7].

The chemicals used in this paper were supplied from Alfa-Aesar and they were used without further purification.

Preparation of Al(III)-pillared calcium bentonites (Al-PCBs)

The preparation of Al-PCBs consists in the following stages: purification of *CaBent-nat*, ion exchange of purified calcium bentonite (*CaBent-pur*) with Cu(II) ions in order to obtain Cu-bentonite (*Cu-Bent*), intercalation of *Cu-Bent* with Al(III)-pillaring agent and calcination of intercalated bentonites (Figure 1). The synthesis of Al-PCBs was realized according to experimental procedure described in detail in our previous papers [8, 9]. The calcination step is very important for the materials conversion into stable pillared clays. The varied calcinations parameters of Al-pillared bentonites are presented in Table 1.

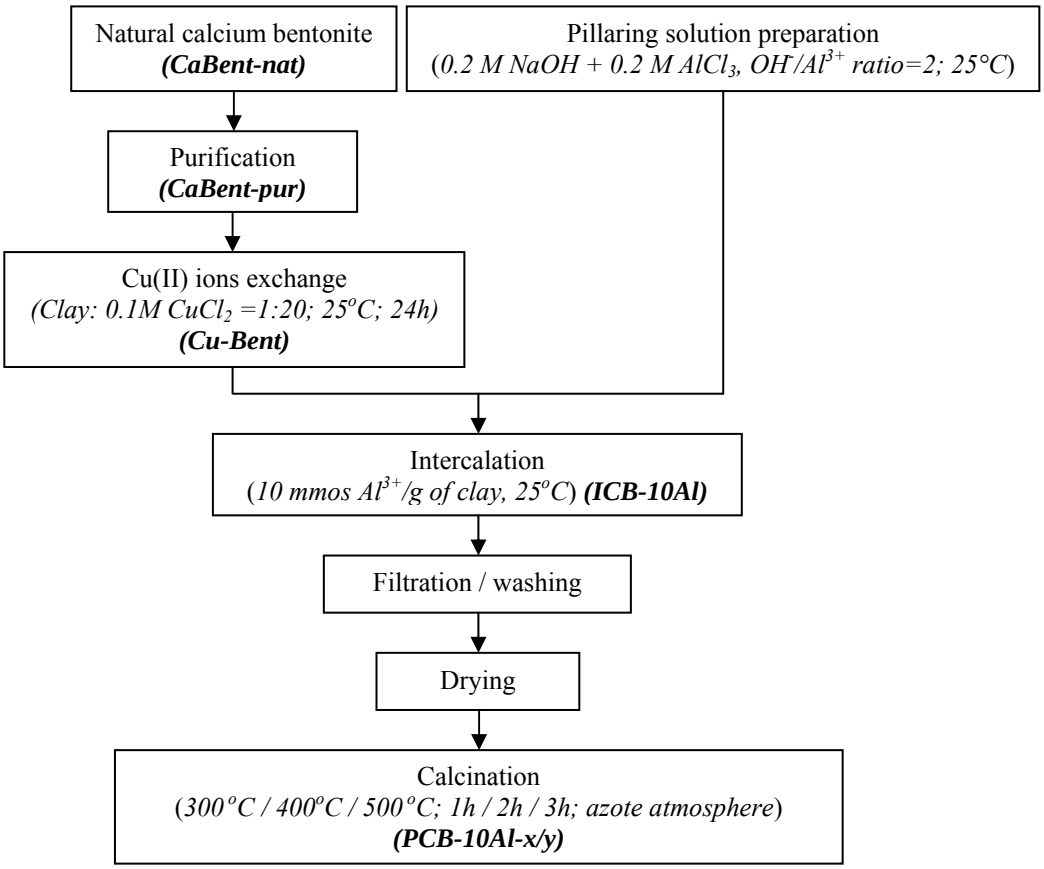


Figure 1. *Synthesis of Al(III)-pillared calcium bentonites*

Table 1. *Varied parameters for synthesized materials*

Material	Calcination temperature [°C]	Calcination duration [min]
PCB-10Al-300/1	300	60
PCB-10Al-400/1	400	60
PCB-10Al-500/1	500	60
PCB-10Al-300/2	300	120
PCB-10Al-400/2	400	120
PCB-10Al-500/2	500	120
PCB-10Al-300/3	300	180
PCB-10Al-400/3	400	180
PCB-10Al-500/3	500	180

Characterization methods

The densities of raw material and of purified bentonite were analyzed using Micromeritics AccuPyc II 1340 apparatus, under argon flow. The particles size of natural and purified bentonites was determined with a laser particle size type Scirocco 2000, Apa model 2000 (Marvern Instruments society), using dry process.
The chemical composition of raw material was measured by X-ray photoelectron spectroscopy (XPS) using a KRATOS AXIS ULTRA DLD apparatus. The excitation monochromatic X-ray source is the Al $K_{\alpha 1}$ whose hν energy is equal to 1486.6 eV. The kinetic energies of photoelectrons are measured by a hemispherical spectrometer (CHA).
The morphological analyses of the materials were realized through scanning electron microscopy (SEM), using a Philips XL30 device and through transmission electron microscopy (TEM), using a TEM JEOL 2012 apparatus. The samples were sputter-coated with Au and Pd under vacuum in an argon atmosphere, using Baltec SCD 050 apparatus, in order to achieve sufficient electrical conductivity. Particle images were obtained with a secondary electron detector. Semi-quantitative chemical analyses of the samples were determined using an EDX device which is coupled with the SEM apparatus.

RESULTS AND DISCUSSIONS

The physical characteristics of natural and purified bentonites are presented in Table 2.

Table 2. *Physical characteristics of natural and purified bentonites*

Sample	Density [g·cm^{-3}]	Diameter [µm]		
		D10*	D50	D90
CaBent-nat	2.38	2.81	18.71	78.84
CaBent-pur	2.24	0.95	2.86	15.95

*D10 - particles size below which 10% of the sample are found
D50 - particles size below which 50% of the sample are found (mean diameter)
D90 - particles size below which 90% of the sample are found

The results obtained for the determination of natural and purified bentonites density confirm that the presented impurities in the *CaBent-nat* were eliminated after the

purification process. *CaBent-pur* density value decreased from 2.38 to 2.24 g·cm^{-3} due to the elimination of cristobalite and quartz, whose densities are 2.33 and 2.65 g·cm^{-3}, respectively [10].

XPS spectrum analysis is presented in Figure 2 and chemical elemental composition is done in Table 3. The semi-quantitative elemental analysis of raw material surface reveals that the largest proportion consists of Si^{2+} and Al^{3+} ions (justification of aluminosilicates term to mineral clays).

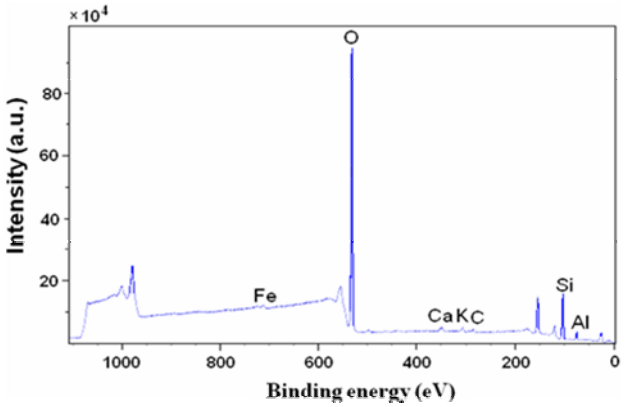


Figure 2. *XPS spectrum for CaBent-nat*

Table 3. *Elemental chemical composition by XPS analysis of CaBent-nat*

Element	Binding energy [eV]	FWHM* [eV]	Raw area [cps eV]	Atomic conc. [%]	Mass conc. [%]
Fe 2p	725.611	7.896	4325.7	1.15	3.16
O 1s	532.421	1.839	59372.1	62.73	49.40
Ca 2p	352.427	2.307	1524.6	0.72	1.42
C 1s	289.635	1.651	1059.4	3.36	1.98
K 2p	296.377	1.804	488.2	0.29	0.56
Si 2p	104.123	1.689	8113.8	23.88	33.01
Al 2p	75.000	1.644	1533.5	7.87	10.45

* full-width half-maximum

The Fe^{2+} cations are also presented in the composition of raw material, being the central cations from the octahedral layers of montmorillonite. In the composition of natural calcium bentonite are presented the Ca^{2+} and K^{+} cations, which are the exchangeable cations from the interlamellar space of montmorillonite. The carbon, which was probably originated from organic impurities, was also identified in the XPS spectrum of bentonite.

Through particle size analysis of raw materials, it is possible to determine the maximum diameters corresponding to the cumulative volume of 10 % (D10), 50 % (D50) and 90 % (D90) of the particles total volume (see Table 2). High values of D90 diameter, for both analyzed bentonites, may come from the tendency of bentonites particles to aglomerate. Two fractions can be distinguished from particles size distribution analysis of *CaBent-nat* sample (Figure 3), which correspond to the following dimension intervals: 0.1 - 18.70 μm (0 - 80 %) and 20 - 200 μm (0 - 100 %). In the case of *CaBent-pur*, the dimension intervals are: 0.1 - 15 μm (0 - 100 %) and 15 - 100 μm (0.5 - 20 %).

The average diameter of natural bentonite particles (D50) is 18.71 μm, in comparison with the purified one, which is 2.86 μm.

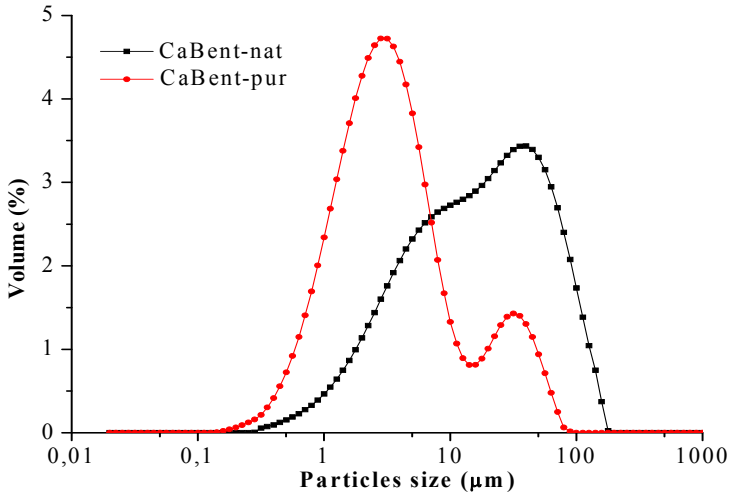


Figure 3. *Granulometric size distribution curves of CaBent-nat and CaBent-pur samples*

Figure 4 shows the SEM micrographs of nanomaterials evolution from raw material to Al-PCB.

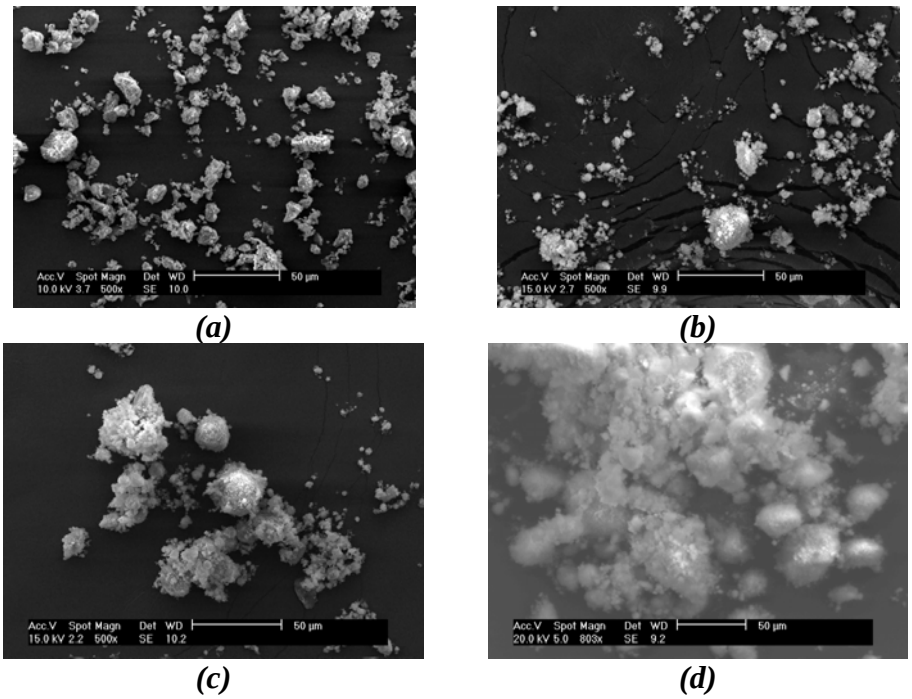


Figure 4. *SEM images for CaBent-nat (**a**), CaBent-pur (**b**), Cu-Bent (**c**) and PILC-10Al-300/1 (**d**)*

The morphological analysis of *CaBent-nat* shows the presence of large clearer particles, due to quartz presence in its structure (impurity in the crude bentonite). After purification (Figure 4B) and Cu(II) ions exchange (Figure 4C), the bentonite particles

are smaller and tend to form aggregates. In the case of pillared material, this has become more porous and fluffy by binding of polyhydroxocations of aluminum in the interlayers of bentonite. Its particles have the tendency to form nanoparticle aggregates, which cannot determine its morphology and particularly its lamellar structure, due to the coalescence of these nanoparticles. The *PILC-10Al-300/1* material predominantly consists in small aggregates of nanoparticles that exhibit a porous structure (Figure 4D). The semi-quantitative chemical analyses of bentonites by EDX are presented in Table 4.

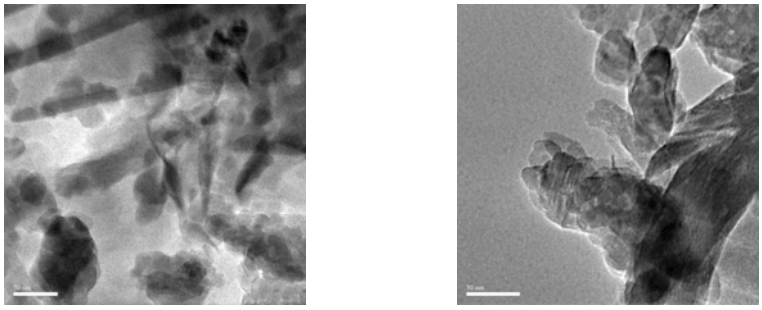
Table 4. *Chemical composition of clays determined by SEM-EDX analysis*

Element	Mass [%]	
	Cu-Bent	*PCB-10Al-300/1*
O	47.57	51.16
Mg	0.04	-
Al	12.72	19.94
Si	32.21	28.58
Fe	0.12	0.04
Cu	7.14	0.26
K	0.06	-
Ca	0.14	0.02

The most abundant components of bentonites, which represent the main components of clay minerals, are Si and Al. The presence of Mg^{2+}, Ca^{2+} and K^{+} can be observed in the case of *Cu-Bent*, these being the interlayer cations between the clays sheets. The existence of Mg^{2+}, Ca^{2+} and K^{+} in low quantity (in comparison with raw material chemical composition presented in a previous paper [4]) together with the higher amount of Cu ions in the composition of *Cu-Bent* sample denotes that Cu ion exchange process has been achieved.

By elemental microanalysis using the energy dispersive X-ray, is observed that after the Al(III)-pillaring process, the amount of aluminum increases considerably. The presence of Cu(II) ions in the composition of *PCB-10Al-300/1* material, indicates that ion exchange between Cu(II) ions and Al(III) polyhydroxocations was not total, in intercalation process of bentonites with pillaring agent.

The TEM micrographs (Figure 5) show more structural informations for the analyzed nanomaterials. The lamellar structure of nanomaterials is clearly observed in comparison with SEM analysis.



(a) ***(b)***

Figure 5. *TEM images for CaBent-pur (100 nm (30000x)) (**a**) and PCB-10Al-500/3 , (50 nm (60000x))(**b**)*

Ca-Bent-pur has a layered sheet structure with a smooth surface (Figure 5A). The morphology of the Al-PILCs was strongly affected by the intercalation of Al-polyhydroxocations into the interlayer of montmorillonite. During the calcination process, the layered structure of the clay was preserved (Figure 5B). The micrographs clearly show that the dimensions of particles are nanoscale, the sizes being under 20 nm. The research results confirm our previous results [8, 9], by which the optimal specific surface area (155 $m^2 \cdot g^{-1}$) and optimal basal distance (1.7 nm) were obtained in the case of calcium bentonite (*PCB-10Al-300/1*), which was calcinated for 1 h at 300 °C in azote atmosphere.

CONCLUSIONS

The chemical microanalysis using the energy dispersive X-ray shows that the Al(III)-pillared bentonites were successfully synthesized. The images obtained by scanning electron microscopy and transmission electron microscopy clearly show that Al-PCBs dimensions are nanoscale (< 20 nm) and tend to form agglomerates. The material with the best characteristics, *PCB-10Al-300/1*, will be chosen in the aim of its using in liquid effluents remediation.

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