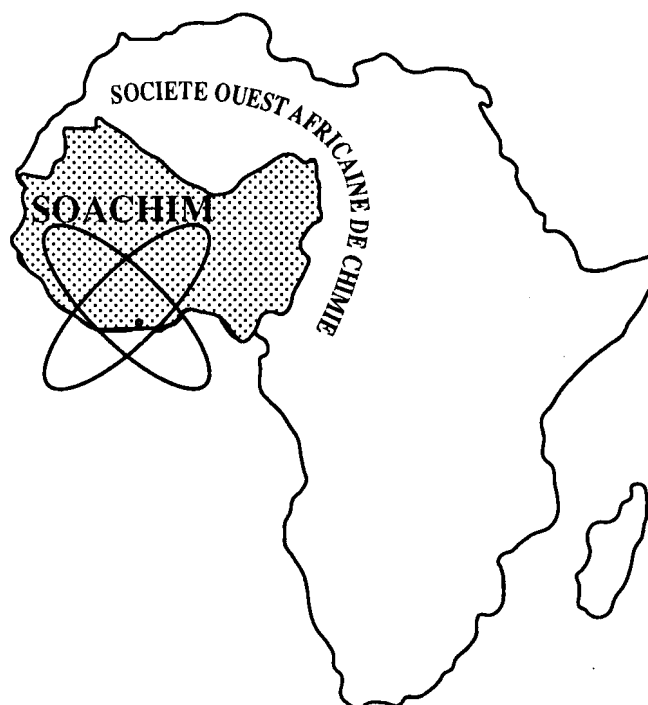


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Synthesis and physico-chemical characterizations of a natural palygorskite-based adsorbent from Allou Kagne in Senegal

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Abstract: Clay minerals are often used as natural adsorbents because of their low cost, large specific surface area and high cation exchange capacity. However, studies have shown that natural clay minerals have some adsorption capacity for anionic pollutants but their adsorption capacity for organic pollutants is low. By modifying natural clay minerals with surfactants, polymers and silane coupling agents, the surface of clay minerals can be transformed from hydrophilic to hydrophobic, and a low-cost, high adsorption performance organoclay adsorbent can be obtained. It can effectively improve the adsorption of clay minerals on hydrophobic organic pollutants. Thus, we are interested in the synthesis and physico-chemical characterization of an adsorbent named (argAlF-3-APTES) from the fraction (argAlF) extracted from natural palygorskite (argAlB) and 3-aminopropyltriethoxysilane organosilane (3-APTES). Several techniques used to characterize the adsorbent, including transform infrared spectroscopy (FTIR), and solid state nuclear magnetic resonance (NMR) of ²⁹Si and ¹³C. The 2921 cm⁻¹ and 2850 cm⁻¹ bands associated with the chemical displacements of silicon atoms of organosilane at -61.97 and -67.04 ppm peaks suggested that the aminopropyl group was successfully anchored on the surface of palygorskite.

Keywords: Palygorskite, Allou Kagne, adsorbent, organoclay,

Synthèse et caractérisations physico-chimiques d'un adsorbant naturel à base de palygorskite provenant de Allou Kagne au Sénégal

Résumé : Les minéraux argileux sont souvent utilisés comme adsorbants naturels en raison de leur faible coût, de leur grande surface spécifique et de leur capacité d'échange cationique élevée. Cependant, des études ont montré que les minéraux argileux naturels ont une certaine capacité d'adsorption pour les polluants anioniques, mais que leur capacité d'adsorption pour les polluants organiques est faible. En modifiant ces derniers avec des tensioactifs, des polymères et des agents de couplage au silane, la surface des minéraux argileux peut être transformée d'hydrophile en hydrophobe, et un adsorbant organoargileux à faible coût et à forte performance d'adsorption peut être obtenu.

Ainsi nous nous sommes intéressés à la synthèse et à la caractérisation physico-chimique d'un adsorbant à partir de la fraction (argAlF) extraite de la palygorskite naturelle (argAlB) et de l'organosilane 3-aminopropyltriéthoxysilane (3-APTES). Plusieurs techniques, dont la spectroscopie infrarouge à transformée de Fourier (FTIR), et la résonance magnétique nucléaire à l'état solide (RMN) du ²⁹Si et ¹³C ont été utilisées pour caractériser l'adsorbant. Les bandes à 2921 cm⁻¹ et à 2850 cm⁻¹ associées aux déplacements chimiques des atomes de silicium de l'organosilane à -61,97 et -67,04 ppm confirme la réaction entre la palygorskite et l'organosilane.

Mots clés : Palygorskite, Allou Kagne, adsorbant, organosilane.

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1. Introduction

The organo-mineral materials are obtained by modification of the surface of clay supports with organic compounds. They have different applications in various fields ^[1]. They can be used as examples in water treatment and added as additives for the preparation of clay polymer hybrid materials or as catalytic supports in organic substance conversion reactions ^[2-5]. Due to the presence of hydroxyl groups on the surface, acid sites of Lewis and Brønsted, interlayer cations, etc., the surface of clays can be modified. Approaches to clay surface modification include grafting and intercalation ^[6-10]. The intercalation refers to a process that a guest molecule or ion is inserted into the inter-layer space by adsorption or ion exchange ^[11]. Grafting is a process that links the inorganic and organic components via strong bonds such as covalent to obtain functionalized clays ^[12,13]. Modification with organosilane involves grafting reactions by establishing covalent bonds between the reactive groups of the layer, normally hydroxyl groups, and silane molecules. These reactions can be restricted to the external surface (the basal spacing remains unchanged) or to the interlayer surface, in which case an interlayer expansion occurs. The resulting material can be defined as a hybrid material or, more specifically, functionalized inorganic layered material ^[13]. There are many types of commercially available silanization agents. They are easy to react with a hydroxylated surface and introduce active groups (e.g., amino group and carboxyl group) to the surface of the material. Palygorskite, also known as attapulgite, is a hydrous magnesium alumina silicate with the theoretical formula $Mg_5(Si, Al)_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ ^[14].

The attapulgites of Senegal are mainly exploited by the Senegalese Phosphates de Thiès Society (SSPT). This company has an industrial operation in Allou Kagne (14°45'44.9"N -17°00'17.6"W) and two open-pit mines in Gagnabougou (Warang) and Sébikhotane. The palygorskites commonly known as attapulgites of allou kagne deposit is dated the hypresien. They are distributed around the horst of Ndiass between Maestrichtien and paléocènes ^[15]. Palygorskite due to its large surface area and the large number of silanol groups on its surface reacts easily with organosilanes ^[16]. Thus the aim of this paper is the synthesis and characterization of an adsorbent based on the fraction extracted from natural palygorskite of allou kagne and 3-aminopropyltriethoxysilane.

2. Experimental

2.1. Chemical reagents

The organosilane grafting agent, the 3-aminopropyltrimethoxysilane (APTES) ($Si(OC_2H_5)_3C_3H_6NH_2$), purity 98%, was purchased from Sigma-Aldrich and used without further purification. Toluene (99.8%) was also provided by Sigma-Aldrich. Other reagents such as NaOH (N98%, granulated) and HCl (37%) from Merck were used for acid treatment and pH adjustments during purification.

2.2. Purification and extraction of the clay fraction

The carbonates are dissolved by attack with dilute hydrochloric acid (1M). The pH above 4.5 is controlled throughout the handling to prevent any attack on the palygorskite structure. Thus 15 g of palygorskite is dispersed in 100 ml of water, then 1 M hydrochloric acid is added drop by drop. After acid attack, the sample is washed several times with distilled water to remove chloride ions (paper pH test) and separated by centrifugation. The palygorskite treated with hydrochloric acid (1M) was saturated with Na^+ by slowly mixing, under stirring, 30g of argAlF powder with 200 ml of NaCl solution (1M). Thereafter, the supernatant was discarded after the mixture settled down and the NaCl solution was renewed. The operation was repeated three times to ensure a complete ion exchange. The aim is saturating the clay minerals intersheet with Na^+ . The Na^+ -saturated clay was then washed several times with distilled water to remove salt excess evidenced by $AgNO_3$ test and to enhance the clay dispersion. After Na^+ homoionisation, the fine clay fraction (<2 μ m) was extracted using standard sedimentation procedures and dried at 80°C ^[17]. The new sample thus obtained is named (argAlF) and used to synthesize the adsorbent.

2.3. Synthesis of adsorbent

1.5 g of the clay fraction (argAlF) was dispersed in 90 mL of toluene under magnetic stirring and Then 7.5 mL of 3-APTES was added dropwise. The dispersion was refluxed and agitated for 24 H. The obtained solid was sequentially washed three times with toluene to remove the non-bonded silane, filtered; and dried for 24H for 70°C. The functionalized sample was termed argAlF-3-APTES.

The silanisation grafting reaction is schematically represented in Figure 1.

2.4. Characterization Methods

The chemical composition of the clay samples was determined by inductively coupled plasma- optical emission spectrometry using an ICP-OES Iris Advantage ERS equipped with a radially viewed torch (Thermo Scientific). Samples were powdered and fused in a Pt crucible with ultra-pure LiBO_2 . After cooling at room temperature, the fused clay was dissolved in 1n HNO_3 . XRD patterns of the kaolinite and modified organo- kaolinite were obtained on a Philips PW 1800 diffractometer using $\text{Cu } -\text{K}\alpha_1$ radiation ($\lambda = 0.15406 \text{ nm}$) and a scanning range $1\text{-}70^\circ 2\theta$ with a step size of $0.02^\circ/\text{s}$. A LEO435VP scanning electron microscope (SEM) equipped with an X-ray energy dispersion spectrometer (EDS) was used to characterize the morphology of clay particles and to perform point elemental analysis. Infrared transmission spectra (IR) were recorded by using KBr pellets on a Bruker IFS 66 IR spectrometer with a DTGS detector and analyzed with OPUS software.

The number of scans was fixed at 32 with a resolution of 4 cm^{-1} . Thermal gravimetric (TG) and derivative thermal gravimetric (DTA) analyses of palygorskite and organo-palygorskite were performed with a TG-DSC apparatus (Setaram TG-DSC 111) under air at a heating rate of 5°C min^{-1} .

^1H decoupled ^{29}Si magic angle spinning (MAS) NMR and ^1H - ^{13}C cross polarization magic angle spinning (CP MAS) NMR spectra were recorded on a Bruker Avance NEO 300WB spectrometer ($B_0 = 9.4 \text{ T}$) operating at 79.460 and 100.577 MHz, respectively. Samples were packed in either a 7 mm (^{29}Si) or a 4 mm (^{13}C) diameter cylindrical zirconia rotor and spun at a spinning frequency of 4 and 14.5 kHz, respectively. For ^{29}Si MAS NMR a $\pi/4$ pulse duration of 1.7 ms with a recycle delay of 60 s was used. Variable contact time ^1H - ^{13}C CP MAS experiments were performed to probe the mobility of the organic moieties in the interlayer space. These experiments were recorded with a proton $\pi/2$ pulse duration of 5 ms, a contact time between 6 ms and 10 ms and a recycle delay of 8 s.

3. Results and Discussion

3.1. Morphological Characterization

The SEM micrographs and EDS analyses of the treated separated fine fraction (argAlF) and the functionalized clay (argAlF-APTES) are represented in figures 2 and 3, respectively. The photograph showed that the samples were composed of many large crystal bundles and few single needle-like crystals. Individual needles were generally assembled in bundles of fibers. The fiber length is between $1.23\mu\text{m}$ and $1.58 \mu\text{m}$ for the fine fraction and a length of $1.58 \mu\text{m}$ is measured for the functionalized clay. This particle arrangement may be due to the low magnitude of net electrostatic charge of the surface, with the van der Waals attraction predominating over the electrostatic repulsion [18]. After sorption, no morphological change is observed between the clay fraction (argAlF) and the functionalized clay (argAlF-3-APTES). The EDS analysis shows the presence of Ti, Ca and Mg probably corresponding to titanium oxide and carbonate impurities (dolomite and/or calcite) (figure 2b.3b). The silver detected at 3 keV originates from the conductive adhesive used to fix the powder on the sample holder. The intense peak of Si could be ascribed both to clay minerals and free silica impurity detected by XRD at figure 4.

3.2. Identification of Phases

The XRD patterns of the raw sample (argAlB), the fine fraction (argAlF), and the grafted sample (argAlF-3-APTES) are presented in figure 4. The three diffractograms are almost identical except for the peaks of calcite in natural clay (argAlB). The reflections observed at 10.62, 6.32, 5.54, 4.54 Å are attributed to palygorskite [19, 20]. The reflections due to quartz (Q), which appears to be the most abundant diluting mineral, were observed at 4.24, 3.34 and 1.81 Å [21]. Nevertheless, any peak related to carbonate impurity can be observed in the fine fraction due likely to their small amounts lower than the detection threshold (<5%).

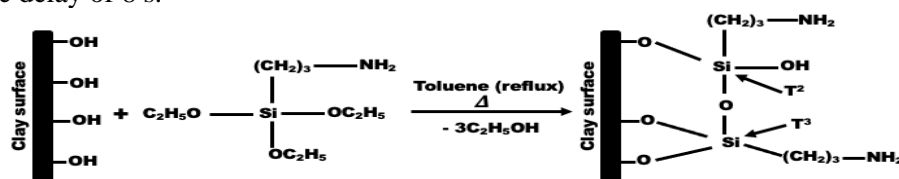


Figure 1: Schematic illustration of functionalization.

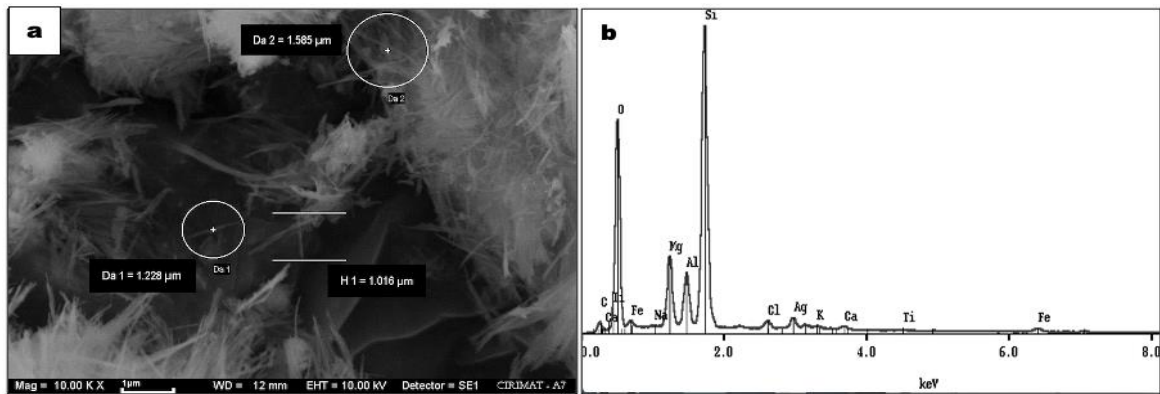


Figure. 2: Clay fraction (argAIF): (a) SEM micrographs and (b) EDS analysis

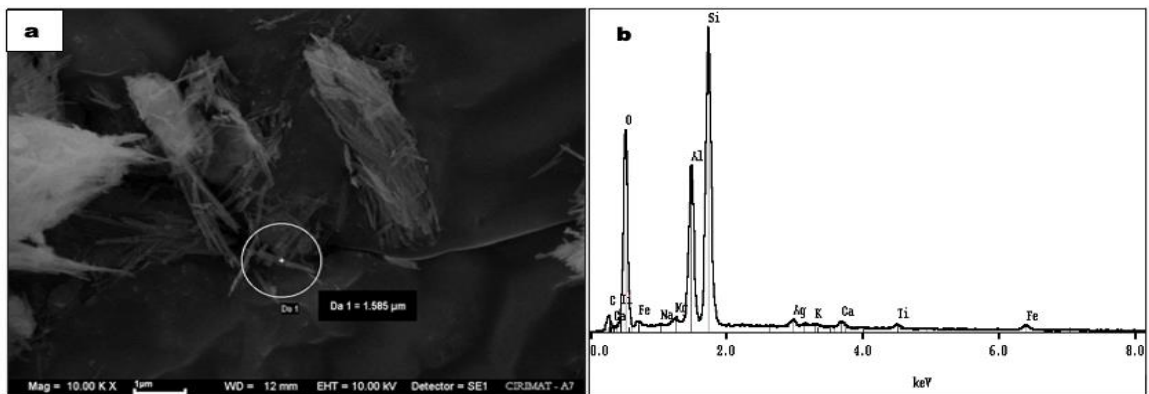


Figure 3. Functionalized clay (argAIF-3-APTES): (a) SEM micrographs and (b) EDS analysis

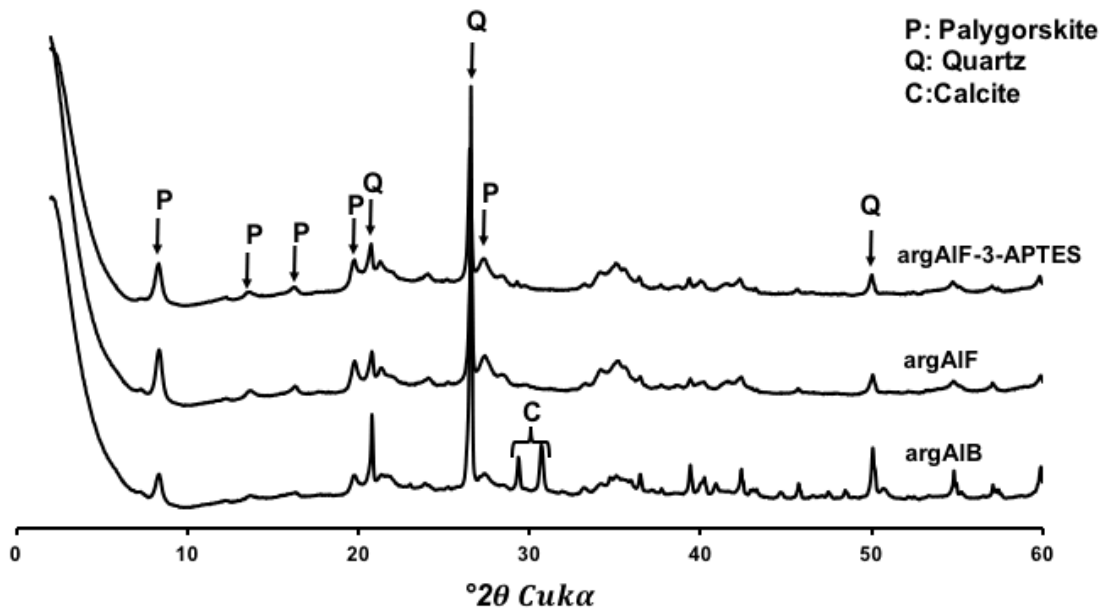


Figure. 4: XRD patterns of the natural clay (argAIB), the fine fraction (argAIF), and the functionalized clay (argAIF-3-APTES)

3.3. Chemical Analysis

Table I shows the chemical composition of the raw clay and of its fine clayey fraction. The results show that the clays are essentially constituted by silica and alumina, the amount of iron oxide is also noticeable while the contents in alkaline and alkaline-earth oxides are low. Except the decrease in CaO content due to the acid treatment the clay fraction has practically the same chemical composition as the raw clay. The noticeable increases in Al₂O₃, Fe₂O₃ and MgO contents indicate that the clay minerals are much concentrated in the separated clayey fraction.

3.4. Adsorption Properties

The adsorption-desorption isotherms of nitrogen do not exhibit significant differences between the separated fine fraction and the adsorbent. It belongs to the type IV (especially visible on the desorption branch) according to the BBDT classification [22]. A summary of the surface properties of all samples is listed in Table II.

The amount of nitrogen adsorbed increased gradually with increasing relative pressure when P/P₀

< 0.35, in which the adsorption and desorption lines completely coincided with each other, indicating a monolayer adsorption. It means that the adsorption of nitrogen occurred mainly in the micropores and formed a nitrogen monolayer [23]. The amount of nitrogen adsorbed increased and small hysteresis loops were observed when P/P₀ > 0.35, indicating the existence of meso and macropores in the palygorskite samples.

Significant changes in nitrogen adsorption-desorption was observed upon grafting, both the specific surface area and the pore volumes decreased after functionalization. This might be due the steric hindrance offered by the propyl groups well within the pore [24]. The increase of the average pore diameter is due to the reduction of microporous contribution

The increase of the average pore diameter is due to the reduction of microporous contribution.

Similar observations have been reported in the study of the functionalization of porous heterostructures by amorphous silica gels grafted with amine and thiol groups [25].

Table I: Chemical analysis of the clay samples (*LOI (loss on ignition))

Clays	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	PF	Total
argAlB	54.72	6.16	3.99	7.09	7.44	0.09	0.26	0.42	0.69	19.39	100.25
argAlF	55.50	11.22	5.00	6.76	0.50	0.06	0.30	0.66	0.27	18.83	99.85

Table II: Specific surface area (S_s), average pore diameter (D_p), total pore volume (V_p)

Clays	S _s (m ² /g)	D _p (nm)	V _p (cm ³ /g)
argAlF	155	9	0.34
argAlF-3-APTES	30	21	0.16

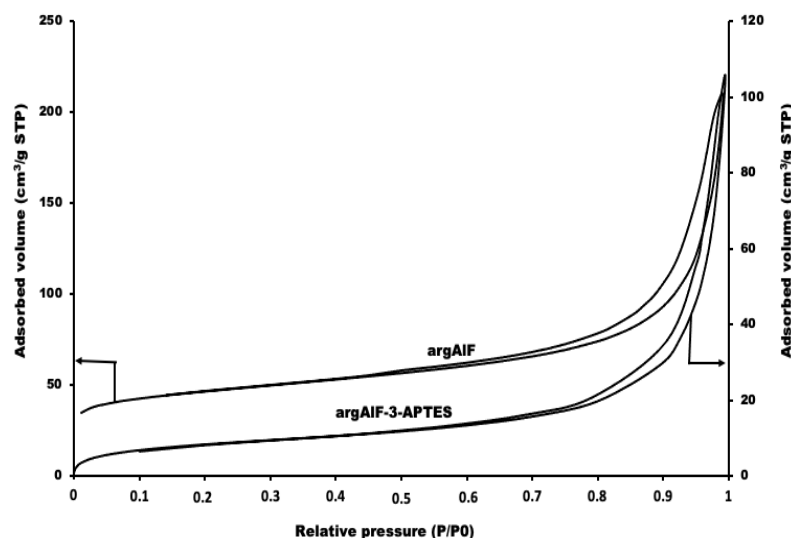


Figure. 5: Adsorption- desorption isotherms recorded for (argAlF) and (argAlF-APTES).

3.5. Infrared Spectroscopy

Infrared spectroscopy is very sensitive to modifications of the clay mineral structure by functionalization. Changes were observed in all frequency ranges of the FTIR spectra.

The Fourier transform infrared spectroscopy (FTIR) of the argAlF and argAlF-3-APTES are shown in Figure 6. The bands at 3612 cm^{-1} and 3562 cm^{-1} of the samples are associated with the stretching vibration of hydroxyl groups which are coordinated to the octahedral magnesium and the tetrahedral silicon. The samples exhibited two bands due to the presence of physisorbed water, namely the $\nu(\text{H-O-H})$ stretching frequency at approximately 3400 cm^{-1} and the corresponding deformation band ($\delta(\text{O-H})$) at 1620 cm^{-1} . In the low energy region, the spectra showed one broad band in the range of $1000\text{--}1200\text{ cm}^{-1}$ with a maximum peak at 1037 cm^{-1} assigned to Si-O and Si-O-Si stretching vibrations, and another bands at 908 cm^{-1} and 468 cm^{-1} assigned to $\text{Al}_2\text{-OH}$ vibration [26,27]. The structure of palygorskite with periodical inversion of apical oxygen in tetrahedral, presents Si-O-Si bond between alternative ribbons. In our samples the band shifts and appears around 1180 cm^{-1} and confirms the presence of palygorskite in the samples. In the organoclay spectrum (argAlF-3-APTES), one may observe aliphatic CH stretching vibrations in the $3000\text{--}2800\text{ cm}^{-1}$ region. The aliphatic CH_2 groups give rise to a doublet at 2921 cm^{-1} and 2850 cm^{-1} , which is assigned to asymmetric and symmetric stretching, respectively [28]. In addition, new peaks at 1562 , 1465 , and 670 cm^{-1} , which correspond to bending vibrations of $-\text{NH}_2$, $-\text{CH}_2$, and deformation of $-\text{CH}$ out of plane [29,30]. All of these vibration bands confirmed the presence of the grafted $-\text{CH}_2\text{-CH}_2\text{-NH}_2$ molecules onto the Palygorskite surface [31].

3.6. ^{29}Si MAS-NMR

Solid-state ^{29}Si CP/MAS-NMR is a reliable method for quantitatively characterizing the nature of various solid surfaces. Regardless of the materials series and their functional group loading, distinct resonances characteristic of siloxane [$Q^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, $n = 2 - 4$] and organosilanes [$T^m = \text{RSi}(\text{OSi})_m(\text{OH})_{3-m}$, $m = 1 - 3$] species could be observed [32]. It can supply the evidence for the anchoring of amino groups. The ^{29}Si NMR spectra of the fine fraction exhibit three main lines at -91.35 (Q^2), -97.43 (Q^3), and -107.47 (Q^4) ppm and a series of sidebands associated with the spinning of

the samples. The two intense resonances at -91.8 and -97.4 ppm are attributed to the silicon atoms in the network and the third chemical value found at -107.47 ppm is attributed to the presence of quartz. In the two sample, the intense singlet around -91 ppm is attributed to a silicon atom linked to two other silicon atoms and one atom aluminum via oxygen atom. The second at -97 ppm is associated with a silicon atom linked to three other silicon atoms via oxygen atom and the three lines at -107 ppm can be attributed to the presence of quartz in the sample confirming traces of this phase even after purification as already revealed by XRD and IR spectra [33].

In addition to the typical resonances of Q^n for the siloxane moieties of the lattice, new resonances for T^2 and T^3 at about -61.97 and -67.04 ppm for argAlF-3-APTES were detected [34].

3.7. ^{13}C MAS-NMR

The ^{13}C CP MAS NMR spectrum of argAlF-3-APTES (Figure 8) displays three signals consistent with previously reported data on similar functionalized silicates. The chemical shifts were assigned by comparison with those observed for the liquid APTES precursor (spectrum not shown) and reported in the literature [35].

No line appeared at -45 ppm corresponding to the chemical shift of Si in liquid (3-aminopropyltriethoxysilane) indicating the absence of free silane molecules physically adsorbed on the argAlF silica surface.

The ^{13}C NMR spectra of argAlF-3-APTES mesoporous materials exhibited sharp, distinct resonance peaks at 12.37 and 26.44 ppm for the carbon atom adjacent to the amine moiety and to the central carbon atom, whereas the carbon atom bonded to the silicon shows a band at 44.37 ppm. The three different carbon chemical environments of the sample were evident from the three distinct peaks. The absence of the signals at 58.2 and 18.0 ppm which we attribute to CH_2 and CH_3 of the ethoxy-group indicates that the precursor underwent a complete hydrolysis [36].

3.8 Thermal Analysis

The TG and DTA curves of the argAlF and the argAlF-3-APTES samples are illustrated in Figure 9. As follows from the literature data, during the heating of palygorskite the molecules of zeolite and coordinately bonded water are removed at temperatures $100\text{--}120^\circ\text{C}$ and $160\text{--}350^\circ\text{C}$, respectively [37].

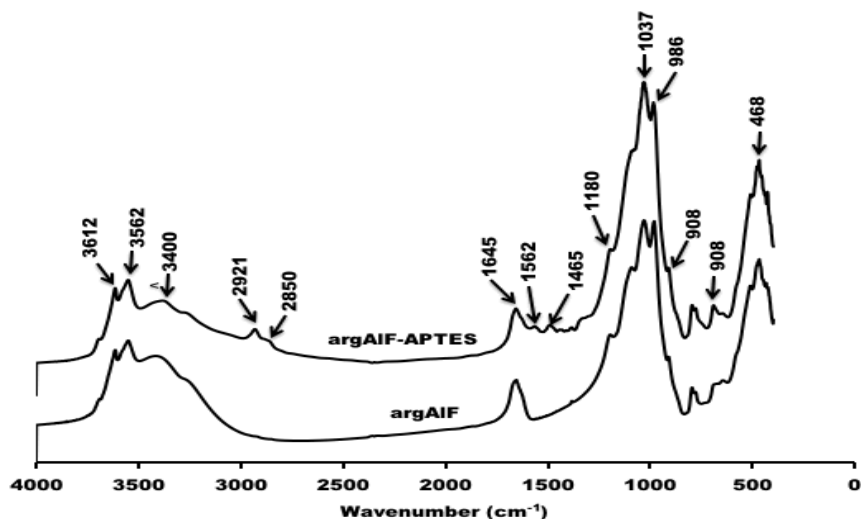


Figure 6: Infrared spectra of the purified sample (argAlF) and the functionalized clay (argAlF-3-APTES).

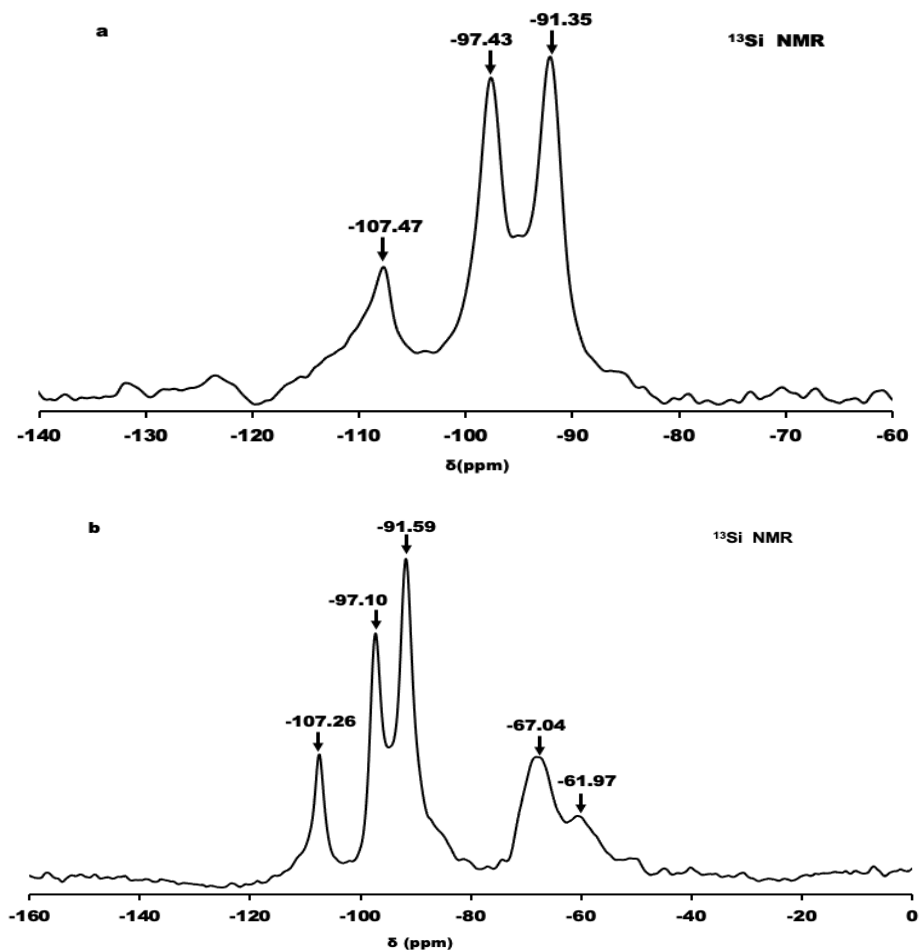


Figure 7: ²⁹Si MAS NMR spectra of the clays: argAlF (a) and argAlF-3-APTES (b)

Unlike the hydrophilic natural palygorskite, the functionalized palygorskite showed evidence of hydrophobicity. The amount of water adsorbed increased from 5.87% to 5.45% for argAlF and

argAlF-3-APTES respectively at 100°C–120°C. Coordination water, bound to octahedral cations, is lost in two different endothermal steps. The first occurs between 160 and 350°C with a mass loss of

~3.23% for argAlF and 3.25% for argAlF-3-APTES and leads to the formation of semi-anhydrous palygorskite. The second loss is in the range of 350-600°C corresponding to the condensation of the two remaining water molecules and, simultaneously, hydroxyl groups. The Weight loss in the step is approximately 5.38% for argAlF. The functionalized sample (argAlF-3-APTES) shows an additional weight loss ~20.67% between 350°C and 600°C, attributed to grafted silane molecules.

The DTA curves revealed the dehydration/dehydroxylation of palygorskite and the decomposition of organic modifiers on the surfaces of palygorskite fibers. Indeed, an endothermic effect is observed occurring at 110 °C and 117 °C. This is due to the removal of physisorbed water and part of zeolitic water filling tunnels [38-39]. Another endothermic peak is observed between 160 and 330 °C at a maximum of 236 °C which is ascribed to the

elimination of the remaining zeolitic water and/or to water coordinated to octahedral edge cations [38]. Between 330 and 590 °C, a broad endothermic effect is observed with a maximum of 496 °C. This peak could be attributed to the loss of the residual coordinated water and/or crystalline water by dehydroxylation of the inner octahedral cations [39]. The non-functionalized clay argAlF displays dehydroxylation at ~472°C and is indicated by a single event while two events have been observed in the case of the modified clays. The characteristic temperatures at which the rate of mass-change is maximum were observed at 436 and 496°C for the argAlF-3-APTES sample. The peak at 436 is attributed to the decomposition of the grafted APTES and the DTA peak centered at 496°C is due to the dehydroxylation of the silicate layers of palygorskite [40].

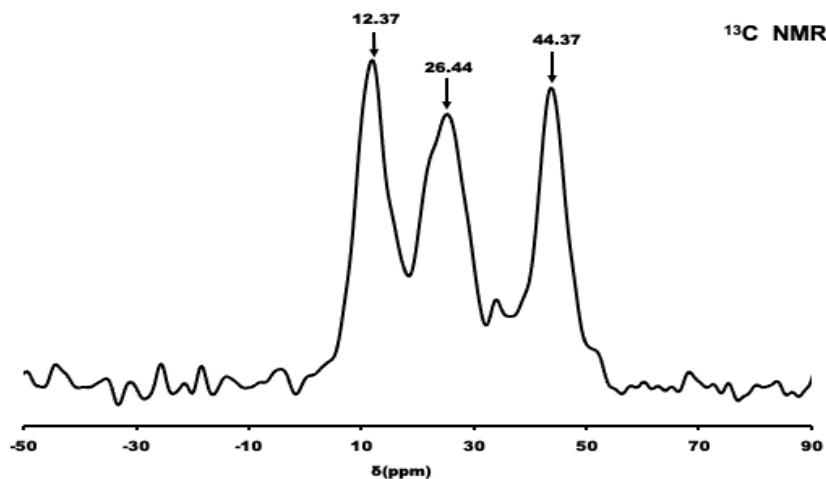


Figure 8: ^{13}C MAS NMR spectra of functionalized clay argAlF-3-APTES

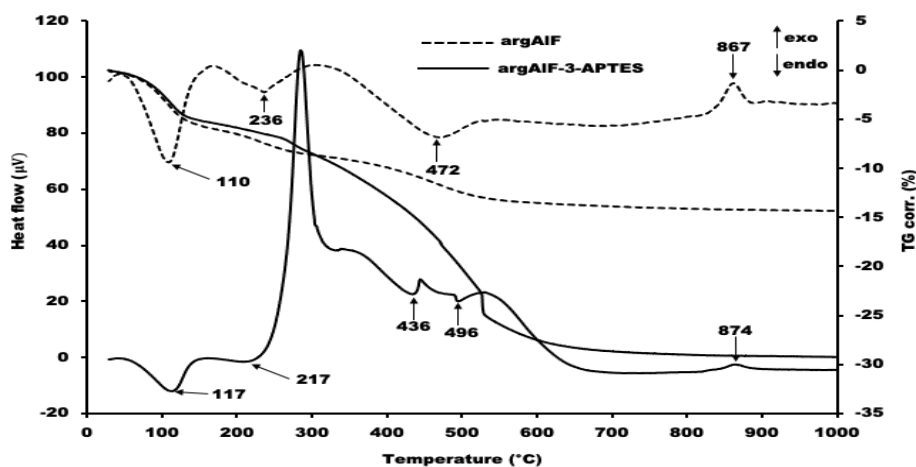


Figure 9: TGA and DTA spectra of the fine fraction (argAlF) and the functionalized clay (argAlF-3-APTES).

4. Conclusion

Palygorskite was functionalized by 3-aminopropyltriethoxysilane (3-APTES) in the high-speed shear process. The XRD patterns combined the FTIR spectroscopy showed that 3-aminopropyl triethoxysilane (3-APTES) is grafted in the surface on the palygorskite. The obtained NMR results gave clear evidence of the grafting of organic molecules on the clay surface and allowed us to identify the grafts and to define their conformations. The presence of T² and T³ in ²⁹Si MAS NMR combined ¹³C MAS-NMR spectra and DTA showed that the hydrolyze was complete. SEM indicated that the reaction produced a continuous coating of individual fibers of palygorskite. The morphology of palygorskite did not change significantly after surface modification. After the modification, the surface properties of the clays are changed and the new adsorbent thus obtained can be used in various fields, such as water treatment and discoloration of natural oils.

5. Acknowledgements

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