

Bentonite Modified with γ - aminopropyltriethoxysilane as Stationary Phase for Thin-layer Chromatography

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The bentonite is a rock of volcanic origin with a high content of montmorillonite. A new polar stationary phase for thin-layer chromatography was prepared from the reaction of γ -aminopropyltrimethoxysilane with bentonite. The surface chemical modifications were determined by elemental analysis, specific surface area measurements, FTIR spectroscopy, thermal analysis and TLC. This product can be employed successfully in chromatographic separations as stationary phase.

Keywords: Chemically modified stationary phase; bentonite, γ - aminopropyltrimethoxysilane, thin layer chromatography, FTIR spectroscopy, thermal analysis

The bentonites are rocks essentially formed from a clay-type mineral resulted from the devitrification and chemical alteration of the glass from the eruptive material, usually volcanic ashes and tuffs [1].

Bentonite is an aluminium phyllosilicate, being natural clay containing a high percentage of montmorillonite, an acid silicate where several Al and Si atoms were replaced with Fe and Mg atoms. Montmorillonite has the following chemical formula: $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2[\text{Si}_4\text{O}_{10}(\text{OH})_2] \cdot n\text{H}_2\text{O}$. Montmorillonite was formed by alteration of basic rocks and pyroclastic materials (glasses, ashes, volcanic tuffs, etc.) in aqueous media with alkaline pH ($\text{pH} > 8$) that was weakly leigated by circulating waters with a high concentration of Mg and Ca and also having a K deficit [2]. They inherit the physical and chemical properties of the primary materials but also display new properties as a result of sedimentary and hydrothermal petrogenesis [3]. There are four common types of bentonites depending on the dominant element, K, Na, Ca and Al [4-9].

This paper describes the synthesis and characterization of a new polar stationary phase for thin layer chromatography prepared from bentonite found in Valea Chioarului (situated at 30 km south of Baia Mare city, Maramures County, Romania) that was chemically modified with γ -aminopropyltriethoxysilane.

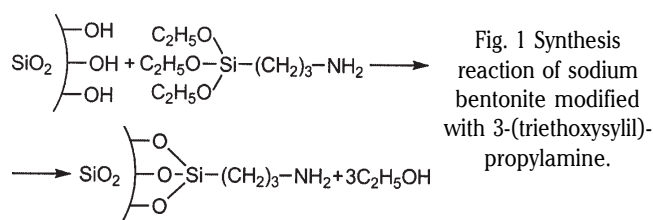
Experimental part

The content of sodium bentonite from Chioarului valley is SiO_2 , 78.12%; Al_2O_3 , 14.30%; Fe_2O_3 , 1.70%; CaO , 0.60%; Na_2O , 1.60%; MgO , 1.60%; K_2O , 1.55%; TiO_2 , 0.50%; MnO , 0.03%. Because the ferric oxide present in bentonite affects its chromatographic properties the purification with HCl of the material is necessary.

By using HCl 6M for purification purposes, the chemical composition was changed, the SiO_2 concentration was increased (from 79.93% to 88.92% due to some soluble

salts such as FeCl_3 , CaCl_2 , NaCl , MgCl_2 , KCl , et all that are removed) and ferric oxide concentration was decreased (from 1.99% to 0.09%) [10]. Sodium bentonite was washed with distilled water (chlorine free), dried and activated at 100°C.

Chemical modification of bentonite with 3-(triethoxysilyl)-propylamine (Merck purity) (fig. 1) was done in a four neck glass balloon including ascendant refrigerant, thermometer and mechanical stirring. The reaction was conducted in nitrogen atmosphere at 60°C. 50 g of purified bentonite and 200 mL of o,m,p-xylene dried on molecular sieve were introduced in this glass balloon. When the temperature of the reaction mass reached 60°C, 11 mL of chemical modifier were added. The silicoorganic mixture was maintained at 60°C for 4 h. The obtained product was washed with xylene, ethylic ether, and methyl chloride and was dried under vacuum. All solvents are of Merck purity as well as KBr powder. The chemically modified bentonite was then characterized by elemental analysis (carbon, nitrogen, and hydrogen), specific surface measurement, FTIR spectroscopy, thermal analysis [11, 12] and chromatographic testing.



Construction of Isotherms

Total surface area (St), pore volume (Vp) and pore radius (Rm) measurements of the samples were obtained by N_2 adsorption-desorption isotherms (measured at -196°C), using the BET model for St determination, and Dollimore –

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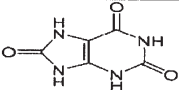
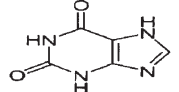
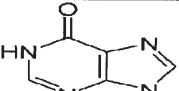
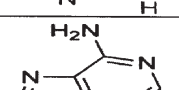
No. crt.	Compound	Structural formulae	$R_F \times 100$	
			Nano-Sil-NH ₂ plates	-NH ₂ chemically modified plates
1	Uric acid		15	17
2	Xanthine		25	28.5
3	Hipoxanthine		38	43.2
4	Adenine		50	63.2

Table 1
VALUES OF $R_F \times 100$ FOR SOME
ORGANIC COMPOUNDS SEPARATED
ONTO NANO-Sil-NH₂ Plates And Plates
With -NH₂ CHEMICALLY MODIFIED
BENTONITE

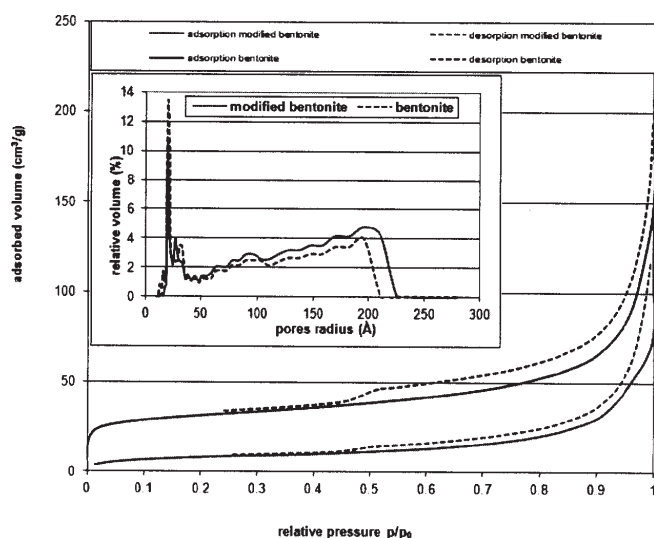


Fig. 2. Adsorption – desorption isotherms of bentonite (upper plot) and amine modified bentonite (lower plot). The inset represents the pores size distribution

Heal method for V_p and R_m . The isotherms were recorded using a Sorptomatic 1990 device (Thermo Electron Corporation). The bentonite sample (approximately 400 mg) was degassed at 200°C for 3h at a pressure of 1Pa prior to determination, in order to remove the physisorbed impurities from the surface. The amine modified bentonite was degassed at 100°C for 6 h. In both cases no pressure variation was observed during 1 h of sample degassing.

FTIR spectroscopy

FTIR spectra were obtained with a JASCO 6100 spectrometer in the 4000-400 cm^{-1} spectral domain with a resolution of 4 cm^{-1} using the KBr pellet technique.

Thermal analysis

The thermogravimetric analysis was performed with a Mettler-Toledo 851° TGA/SDTA Thermal Analysis System, setup in the 25-1100°C domains with a heating speed of 5°C/min in nitrogen atmosphere with a flow of 2 L/h.

Alumina crucibles were used and sample amount analyzed was 17 mg and 16 mg, respectively.

Chromatographic study

The -NH₂ chemically modified chromatographic plates were used to separate several organic compounds (purine derivatives) of Fluka purity (table 1).

Standard solutions (0.1%) of the four compounds were applied to -NH₂ chemically modified bentonite plates and to Nano-Sil-NH₂ (Mackerey-Nagel, Duren) silica gel plates in volumes of 5 μL /spot using a Hamilton syringe.

The development of the plates was done using ascendant technique at room temperature in a non-saturated chamber. A mixture of ethanol-water saturated with NaCl (80:20, v/v) was employed as a mobile phase. The visualization of the separated compounds was realized in UV light at 254 nm with a UV Vilber Lourmat lamp (France).

Results and discussions

Surface area and porosity

The adsorption – desorption isotherms of both samples (unmodified and NH₂- modified bentonite) have very similar profiles (fig. 2). The adsorption isotherms were of type II. The desorption branch presented a H4 type hysteresis combined at high pressures with H3 type. The H4 hysteresis is usually associated with aggregates of plate particles giving rise to narrow slit-like pores [13]. The narrow pores of the analyzed samples (with a maximum situated at $R = 20 \text{ \AA}$ - fig. 2) coexisted with larger ones, as was suggested by the long vertical hysteresis presented at very high p/p_0 values.

The surface area and total pores volume are presented in table 2.

The amine modified bentonite had a much smaller total surface area and half the total pores volume than the unmodified bentonite. The shape of the pores size distribution was not very different for bentonite and amine modified bentonite. For bentonite approximately 13% of pores were small mezopores with $R_m = 20 \text{ \AA}$ and the rest of the pores presented a very large radii distribution

Stationary phase	Carbon/%	Hydrogen/%	Nitrogen/%	$S_{\text{BET}}/\text{m}^2\text{g}^{-1}$	$\alpha/\mu\text{molm}^{-2}$	$V_p/\text{cm}^3\text{g}^{-1}$
Sodium bentonite	-	-	-	111.6	-	0.10
NH ₂ - modified bentonite	3.99	1.52	1.56	30	3.64	0.05

S_{BET} – specific surface area; α – coverage degree; V_p – pore volume

Table 2
SURFACE COVERAGE DENSITY OF
THE SODIUM BENTONITE
UNMODIFIED AND CHEMICALLY
MODIFIED WITH 3-
(TRIETHOXYSYLIL)-PROPYLAMINE

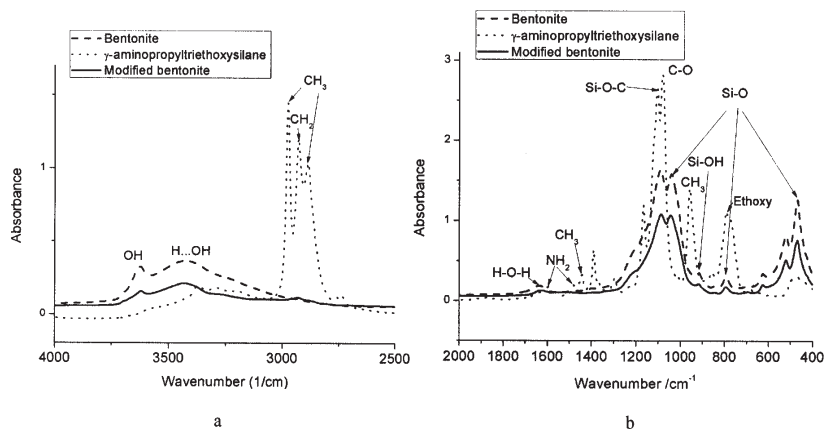


Fig. 3. FTIR spectra of unmodified sodium bentonite (dashed line), 3-(triethoxysilyl)-propylamine (dot line) and of -NH_2 chemically modified bentonite (solid line): a - 4000-2500 cm^{-1} spectral range; b - 2000-400 cm^{-1} spectral range

(between 50 and 210 \AA^2) with a maximum located at 195 \AA^2 . For the chemically modified bentonite the proportion of smaller pores was lower (approximately 10.5%), the rest being distributed in the whole mesoporous domain, with a maximum at 200 \AA^2 . The lower proportion of small pores was consistent with the decrease of surface area observed for modified bentonite.

Density coverage

The results of elemental analysis, the coverage density, the specific surface area and pore volume are presented in table 2. The presence of carbon and nitrogen in the modified bentonite composition showed that the modifier was chemically bonded to bentonite. The diminishing of the specific surface area and of the pore volume indicated that γ aminopropylsilyl was bonded to the bentonite.

The coverage degree ($3.64 \mu\text{mol}/\text{m}^2$) was in agreement with the literature values [14].

FTIR spectroscopy

The effect of bentonite silanization with 3-(triethoxysilyl)-propylamine consisted on the reduction of surface-OH groups number, the introduction of $\text{-CH}_2\text{-}$ groups from organosilane and the presence of -Si-O groups. Figures 3a and 3b present FTIR spectra of sodium bentonite coming from Valea Chioarului (dash line) and of -NH_2 modified bentonite (solid line). Some surface changes were observed by comparing these spectra, as a result of the silanization reaction:

- the presence of methylene groups from the n-propyl chain of the modifier was evidenced by new band characteristic to $\nu(\text{CH})$ at 2928 cm^{-1} that was not present in the spectrum of the unmodified bentonite;

- the bands at 3654 and 3434 cm^{-1} suggested the presence of adsorbed water (free OH groups) and of crystallization water, respectively;

- an important decrease of broad bands' intensities [$\nu(\text{OH}\dots\text{O})$ at 3434 cm^{-1} and $\delta(\text{OH}\dots\text{O})$ at 1633 cm^{-1} (being also shifted to 1628 cm^{-1}) was observed;

- NH_2 -stretching bands of silane (located in $3400\text{-}3000 \text{ cm}^{-1}$ spectral domain) are overlapped by O-H...O stretching, being difficult to be separated;

- the increase of the Si-O bonds variety was reflected in the $\nu(\text{Si-O})$ and $\nu(\text{Si-O-H})$ bands changes observed in the $1300\text{-}900$ and $600\text{-}400 \text{ cm}^{-1}$ spectral ranges.

Thermal analysis

The bentonite minerals exhibit three stages of thermal decomposition caused due to decomposition of adsorbed water, release of inter layered colloidal water and the compositional water.

First stage of thermal decomposition of unmodified bentonite occurs at about 70 to 280°C due to loss of adsorbed water. In this range, the sample loses a significant part of his weight (7.2%, fig. 4).

The second stage occurs at temperature range 280 to 400°C due to the dehydration of colloidal and entrapped water within the inter atomic layer of unmodified bentonite mineral.

Third stage of thermal decomposition caused due to dehydration of the compositional water occurs at 400°C and finish at 750°C when mass loss is completed (2.7%). This temperature range is also for the decomposition of non-bentonitic minerals like illite and kaolinite. In this temperature range W-shaped peak appears (on DTG) which is mainly due to decomposition of bentonite mineral, illite and kaolinite at slightly close interval of temperature. The decompositional temperature for these minerals is at about 400 to 500°C for illite, 500 to 600°C for kaolinite and slightly above 600°C for bentonite minerals [15].

Chemically modified bentonite was thermally activated before organosilanization and therefore presents a small loss (4.3%) in two steps in 60 to 230°C range, due to loss of adsorbed water (fig. 5).

In the $230\text{-}300^\circ\text{C}$ range, dehydration of entrapped water within the inter atomic layer occurs and approximate the same weight as unmodified bentonite is lost (1.1%).

Third step of the thermal decomposition in $300\text{ to }720^\circ\text{C}$ range shows a substantially mass loss of 8.5%. This is probably due to the burning of organic part (γ -aminopropylsilyl) at 411°C , besides dehydration of the compositional water and partial decomposition of bentonite.

In the last step until to 1100°C , the mass loss is 1.1% and it explaining advanced decomposition of chemically modified bentonite with formation of new phase of metasilicate around at 921°C .

Chromatographic behaviour

Chemically modified bentonite with γ -aminopropyltriethoxysilane is a powder with a white degree of 93% which allows the detection of the thin layer chromatographic separated substances. In order to verify the chromatographic behavior of the -NH_2 chemically modified bentonite, thin layers of 0.3 mm thickness were prepared onto glass plates of $10 \times 10 \text{ cm}$. The deposited paste was prepared by mixing four parts of Ba and Mg aluminate activated with europium ($\text{BaMg}_2\text{Al}_6\text{O}_{27}:\text{Eu}$), three parts of yttrium aluminate activated with cerium ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$), 100 parts of -NH_2 chemically modified bentonite powder and a binder consisting of 2.5 parts polyvinyl alcohol and a part of agar-agar solved in warmed distilled water [16, 17].

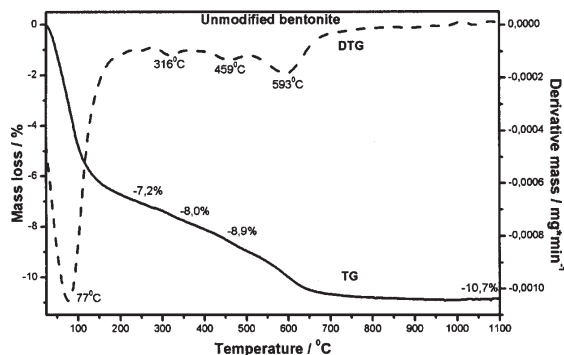


Fig. 4. Thermogravimetric and derivative thermogravimetric curves for sodium bentonite from the Chioarului valley: TG-solid line; DTG-dashed line.

All four compounds were well separated (table 1). The RFx100 values for 3-(triethoxysilyl)-propylamine chemically modified bentonite were higher than those obtained by using Nano-Sil-NH₂ silica gel plates. The bentonite surface was smaller than the silicagel one. This fact didn't hinder the chromatographic separation process. The new obtained product could be successfully used as polar stationary phase in liquid chromatography.

Conclusions

The number of free or hydrogen bonded OH groups diminished after the chemical modification with γ -aminopropyltriethoxysilane as was established by FTIR spectroscopy. This fact could be observed also from the specific surface area diminishing of the chemically modified bentonite. The TG data also evidenced the chemical modification of the bentonite. The bentonite coming from Valea Chioarului, due to its chemical composition, can be used as stationary phase in liquid chromatography, having similar properties as those of the chromatographic silica gel and being cheaper and more easily obtained.

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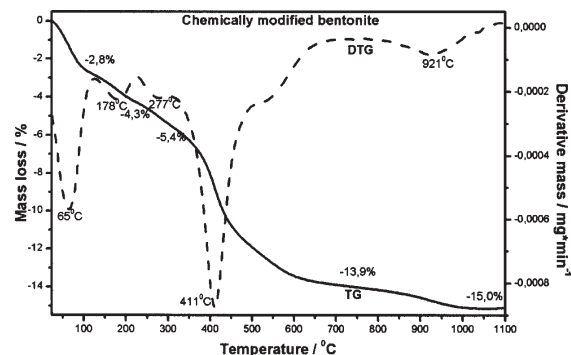


Fig. 5. Thermogravimetric and derivative thermogravimetric curves for -NH₂ chemically modified bentonite: TG-solid line; DTG-dash line

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