Adsorption of essential oil components of *Lavandula Angustifolia* on Pillared modified bentonite

M. EL MIZ *, S. SALHI , A. EL BACHIRI[1], J.P. WATHELET and A. TAHANI[1%]

1 : LACPRENE, Bloc de recherche 2ème étage, Faculté des Sciences Oujda, Université Mohamed 1er;
Route de Sidi Maâfa ; BP 524-Oujda- Morocco
2: Gembloux Agricultural Faculty – FUSAGx. Unité de Chimie générale et organique. Passage des Déportés 2. B-5030 Gembloux (Belgium).
* elmiz.mohamed@gmail.com
[%] abdesstaha@yahoo.fr

Abstract

The aim of this work is the valorization of *Lavandula Angustifolia*. by chemical characterization, and study of the formulation created by the adsorption of active components of Lavandula angustifolia essential oil on sodium modified bentonite. Essential oils were obtained from dried leaves of Lavandula angustifolia; they were extracted by hydro distillation and were analyzed by GC–MS and GC-FID. The hydrodistillation of the areal parts provides essential oil, (9.19 %) of Alpha Thujone, (19.81 %) of 2-Beta Pinene and (23.42 %) of 1,8 Cineole were found to be the major components. The Retention Indices (RI) were calculated for each detected component. Besides, the characterization of the individual components making up the oils was performed with the use of a Mass Spectrometry (MS) library. The quantitative analysis was made by Gas, Chromatography Flame Ionization Detector (GC-FID). The identified components accounted for more than 98% for each essential oil. The results of these studies shown that organic contaminant adsorption is dependent, to some degree, on solid-liquid ratio and the competition system of mixture. The adsorption amount of terpenics and the others components could be the results of many factors. The selectivity was affected by the abundance of each component in the crude essential dependent on the particle size fractions; the finer fractions adsorbed higher amounts. The selectivity of adsorption was affected by the polarity of terpenic components.

Key words: Clays - Bentonite – Essential oil - Adsorption- Lavande angustifolia

1. Introduction

Lavandula angustifolia is an important member of Lamiaceae family. It is an indigenous plant of the Mediterranean south region, tropical Africa and the southeast regions of India. The genus includes annuals, herbaceous plants and small shrubs, having aromatic foliage and flowers.

It is cultivated in France, Spain and Italy. Among these plants, the most common species believed to have medicinal value are Lavandula dentata, Lavandula angustifolia, Lavandula latifolia, Lavan-dula intermedia, Lavandula stoechas and Lavandula dhofarensis[1]. Lavender's essential oil is popular as a complementary medicine in its own right and as an additive to many over the counter complementary medicine and cosmetic products[2]. These have been used for centuries as a therapeutic agent, with the more recent addition; the essential oils derived from these plants were widely used as an antibacterial in World War I[3].

Lavandula essential oils are obtained from the flowering tips of the plants Lavandula angustifolia (lavender). These essential oils have a popular and easily recognisable fragrance. Pure Lavandula angustifolia essential oils are used in aromatherapy, and are thought to have calmative, anti-flatulence, and anti-colic properties[4].

Lavandula essential oil contains various components depending on the species, but there is usually linalyl acetate and linalool, geraniol, 2-Beta Pinene, cineol, coumarin and ethylamyl-cetone (behind its refreshing scent).

The aim of this work is the adsorption study of active components of Lavandula Angustifolia essential oil on sodium modified bentonite to prepare new formulations for cosmetics and medcine containing essential oil and modified clay (prepare new clays with medical and cosmetics propritées) in a way that these effects remain for a long duration of use[5].

Because of the higher volatility of essentials oils, the duration of their activities is very short. The local material suitable for the formulation of the essential oils seemed to be a modified Bentonite type clay. It is cited as good adsorbent and is currently used in medicine, in cosmetics and in other insecticide. Yet, there are no adsorption studies of terpenic compounds on this clay material.

Purified bentonite was used as reference in the preparation of pillared bentonite. These different matrices were characterized before and after modification by X-ray diffraction, nitrogen adsorption-desorption, infrared spectroscopy in Fourier transform, and differential thermogravimetric analysis. It follows that the characterization of the sample of the support is mainly composed of montmorilonite.

In recent years, material sciences have involved the studies related to the production of materials

having a controlled pore structure and improvement of porous materials found in the nature. The production principle is to hold the inorganic layers a part from each other, introducing a bulky guest agent between them. When the used materials are clay minerals, the resulting materials after pillaring are called Pillared Layered Clays (PILCs). The host solid and the production conditions have rather important effects on the quality of the product. Due its high cation exchange capacity, swelling properties, and large sheets, montmorillonite type clay have an important place in the production of pillared clays.

2. Materials and methods

2.1. Plant material (Lavandula angustifolia) and hydrodistillation procedure

The air dried material (200 g) was hydrodistilled in a Clevenger like apparatus for 2 h and the essential oil was collected and analyzed by GC–MS.

2.1.1. Chromatographic analysis of essential oil

The **GC-MS** analyses were done using a **HP-6890 Series II** instrument equipped with Agilent **19091S-433** and **HP-5** capillary columns (30 m 0.25 mm, 0.25 um film thickness), working with the following temperature program: from 60 °C for 1 min to 240 °C for 10 min hold time, ramp of 10 °C/min up to 220 °C; injector and detector temperatures 280 °C; injector Split/splitless N°7673, detector MSD (transfer line heater), carrier gas Helium (1.2 ml/min); with splitless mode and the pressure in the column was 0.629 Bar.

Quantitative results were obtained using **GC-FID**, **HP 6890 Series**, with the same type of column, the same parameters and the same temperature program. The detector temperature was 300 ° C, the hydrogen and air flows rate are 30 ml / min and 450 ml / min.

The identification of the compounds was made by comparison of the retention time (Rt) and Kovats indices with respect to a series of n-hydrocarbons. The relative proportions of the constituents of essential oils are obtained by **GC-FID**, Table.1 shows the chemical composition of the essential oil of lavender, and the percentage of each compound[5].

2.2. Preparation of the sodium pillared bentonite

The bentonite used in this study is a bentonite rich with montmorillonite clay type that was provided from the region of Nador (north-est of Morocco) and used in a purified forme.

Bentonite clays were homoionized with a NaCl solution 2 M, with a solid: liquid ratio of 1/50 (10 g clay/500 mL NaCl). The ion exchange was realized at 25°C and was repeated three times. After each process, the clay was washed with distilled water until no chloride ions were found. To avoid the rapid

evaporation of the water, the ion exchanged samples were slowly dried at 35 °C for 24 h[6]. A portion of the sample was used to prepare pillared-bentonite.

The simplified pillaring method proposed in this paper was carried by intercaling of the pillaring agent in a aqueous sodic clay suspension 5 % (% mass.), ageing, washing, drying and calcination of the intercalated clay at 350 °C.

The pillaring solution containing $[Al_{13}O4(OH)_{24}(H_2O)_{12}]^{7+}$ cations was obtained by adding 250 ml of AlC_{l3} (0.4 M) stepwise to 550 ml of NaOH (0.4 M) . The final neutralization ratio which is defined as $[OH]_{tot}/[Al(III)]_{tot}$ was 2,4 and the solution was agitated for 12 h at room temperature. The resultant solution of pH = 4.5 was added to the clay suspension 2% (1 g clay/100 ml H_2O) and stirred for 6 h at room temperature. The pillared clay form was then centrifuged, filtered, and dried at 60°C in air. Calcination was performed at 350°C for 6 h. The degree of intercalation of the pillaring cations was determined by XRD, by analyzing variations of d(001) in oriented clay-aggregate specimens[7].

2.3.   Characterization

The natural samples purified and modified clay are subjected to analysis and identification by X-ray diffraction (XRD), infrared spectroscopy (IR) and Thermal analysis.

X-ray diffractograms were recorded in a Shimadzu XRD diffractometer D6000 stations working on the monochromatic copper K 1 radiation (1.54 Å). **Figures ١**.

The textural characteristics of clays before and after pillaring were determined from N_2 adsorption/desorption isotherms at 77°K using micrometrics ASAP 2000 volumetric adsorption–desorption apparatus and surface Area and Pore size Analyzer **Figures ٢**. The surface areas were calculated using the multi-point BET method, and a relative pressure (P/P_0) between 0,00095 and 0,9917 was applied.

Infra Red (I.R) spectra were acquired using a Shimadzu Fourier Transform spectrometer over a range varying from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}, and the samples were prepared in the form of a dispersion in a vial KBr (1/200 by weight) **Figures ٣ & ٤**.

Thermal analysis was carried out in a SHIMATZU D6000 coupled to a DC ampler and temperature controller. Data from DTA-TG were obtained in all cases at a heating rate of 5°C/min between 30 and 1000°C and under N_2 atmosphere **Figures ٥ & ٦.**

2.3.1 Adsorption studies

Adsorption of essential oil by the different bentonite fractions was carried out in batch. Increasing amounts of clay fractions (0.03 ; 0.067 ; 0.093 ; 0.121 ; 0.159 ; 0.206 g) were dispersed in 2 ml oil solution (0.754 mg of oil in 2 ml of solution) and equilibrated in an overhead shaker at room temperature (19 °C) for 3 h. The particles were allowed to settle and were separated by centrifugation. The essential oil concentration in the supernatant was determined by GC-FID.

2.3.2 Adsorption isotherm

Adsorption isotherms were determined using the peak area of each component of the essential oils (Nguemtchouin, et al., 2009). The adsorbed percentage was calculated as:

$$\% \ adsorbed = \frac{100(A0 - Ax)}{A0} \qquad \textbf{eq : 1}$$

where A_0 is the peak area of each oil component in the initial solution; A_x the peak area of each component in the supernatant.

The Mass concentration of each compound in the initial essential oil has been determined by depending on the peak area of the internal calibrated (BHT).

$$C(\mu g/ml) = \frac{A0 \times Ae}{me} \qquad \textbf{eq : 2}$$

where A_0 is the peak area of each oil component in the initial solution; A_e the peak area of internal calibrates in the initial solution; m_e mass of the internal calibrated (in 2 ml of initial solution of essential oil).

The amount of each compound adsorbed by clay fractions is:

$$Qn(\mu g/g) = \frac{(ci - cf) \times V}{mc} \qquad \textbf{eq : 3}$$

The percentage of each oil component in the initial solution was calculated as:

$$\%C = \frac{cx}{Ceo} \times 100 \qquad \textbf{eq : 4}$$

where C_i is the concentration of each component in the initial solution and C_{eo} is the concentration of the essential oil in solution. The equilibrium concentration was calculated as:

$$Ce(\mu g/ml) = \frac{Ax}{A0} \times \frac{meo}{Veo} \times \%C \qquad \textbf{eq : 5}$$

where V_{eo} is the volume of solution (ml).

3.   Results and discussion

3.1. Identification of the compounds

The identification of the compounds was made through a comparison of retention time (Rt) and Kovats indices with results obtained by GC-FID[5].

Table: I. Identification results of the components and the percentage of each compound in essential oil

Product Name	Rt	Surface	µg/ml	KI	%in samples	% Adsorbed
Alpha Pinene	10.09	282.35	24.43	942	6.05	100
Camphene	10.40	33.98	2.940	957	0.72	100
Verbenene	10.52	10.88	0.94	963	0.23	100
Sabinene	10.92	22.11	1.91	982	0.47	100
2-Beta Pinene	10.98	924.1	79.96	985	19.81	98,31
Limonene	11.89	29.03	2.51	1033	0.62	87,03
M-Cymene	11.97	99.10	8.57	1038	2.12	92,22
1,8 Cineole	12.03	1092.38	94.52	1041	23.42	57,81
Cis Linalol oxide	12.75	42.67	3.69	1082	0.91	100
Alpha Thujone	13.04	428.84	37.107	1097	9.19	100
L-Linalool	13.17	155.95	13.49	1105	3.34	100
(+) Carvone	13.25	9.156	0.79	1110	0.19	100
Perille Alcohol	13.35	11.85	1.02	1117	0.25	100
(Z E) Alpha Farnesene	13.46	79.02	6.83	1124	1.69	100
Fenchol	14.31	65.198	5.64	1157	1.39	100
1-Methyl adamantane	14.38	5.557	0.480	1183	0.11	100
Cryptone	14.47	30.81	2.66	1189	0.66	100
1-Alpha Terpineol	14.57	21.28	1.841	1195	0.45	100
Alpha Campholene Aldehyde	14.67	40.32	3.48	1201	0.86	100
Camphor	14.78	215.14	18.61	1209	4.61	100
1-4-Terpineol	14.99	17.09	1.478	1224	0.36	100
Verbenone	15.08	11.12	0.96	1230	0.23	99,22
CuminicAldehyde	15.42	19.82	1.715	1255	0.42	100
(+) Carvone	15.46	15.34	1.327	1258	0.32	100
(-) Alpha CampholenicAcid	15.58	7.99	0.69	1266	0.17	100
Trans Alpha Bergamotene	18.05	21.94	1.89	1397	0.47	100
Trans Beta Farnesene	18.68	9.96	0.86	1502	0.21	100
Beta Selinene	18.78	31.45	4.082	1509	1.01	100
Beta Bisabolene	18.93	15.68	2.03	1523	0.5	100
Calarene	19.07	11.02	1.43	1535	0.35	100
1s Cis Calamenene	19.18	14.86	1.92	1545	3.91	100
Cis Alpha Bisabolene	19.32	24.11	3.13	1556	0.62	100
4,7 Dimethyl-1-Tetralone	19.46	5.86	0.76	1568	0.104	100
Beta Eudesmol	20.71	7.29	0.94	1678	0.23	48,22
14-Norcadin-5-En-4-One Isomer B	21.16	5.44	0.707	1707	0.17	91,73

Chromatographic analysis showed that lavender essential oil contains more than 50 components, 35 major compounds of lavender essential oil were selected (the most major components: 1,8-cineole 23.42 % and 2-Beta Pinene 19.81 %) mono terpene hydrocarbons, MH, (-thujene, -pinene, sabinene, -pinene, limonene…), oxygenated mono terpenes OM (Beta Eudesmol, Cis Linalol oxide, 1,8-cineole……), sesquiterpene hydrocarbon ST, ((+) Carvone, Calarene, Cryptone, Verbenene……).

23% (94 ug / ml) of 1,8-cineole and 19.81% 2-Beta Pinene (79.96 ug / ml) in the essential oil, which give important effects such as: antiseptic properties and for the treatment and relief of rheumatic pain (such as external appication formulation: clay powder and essential oil of lavender).

3.2. Characterization of the support:

The major element composition of the investigated clay mineral is presented in Table 2 as % oxides. The main components are SiO_2 (61.17%) and Al_2O_3 (15.13%), with the exception of hectorite, which contains ~ 6% MgO, 4% CaO, Fe_2O_3 (3.25%) and other elements present in minor amounts (K_2O, SO_3, CuO, TiO_2, ZnO). A small percentage of organic matter (MO = 1.08%) and a percentage of water estimated to ~ 10.56%. The fine fraction (2 µm) was purified and sodium exchanged[5,7].

The surface areas and the pore volumes of the samples: Specific surface S_{BET} = 83.5 m²g^{-1}, total pore volume V_t = 0.213 cm^{3}g^{-1}, External specific surface S_{ext} = 81.024 m²g^{-1}. Its cation exchange capacity, determined by adsorption of a copper ethylene di-amine complex[8], is 107 meq/100 g (ignited) clay. Chemical analyses of the samples are given in Table I.

Table II: Chemical composition (wt %) of sodium modified and Raw bentonite

Oxides	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O_2	K_2O	SO_3	CuO	TiO_2	ZnO
Na-B	61.17	15.13	4.00	6.00	3.25	1.1	0.52	0.38	0.13	0.12	0.1
Raw-B	64.05	16.33	4.13	6.69	3.44	1.12	0.65	0.37	0.09	0.1	0.05

3.2.1   X-ray diffraction

The **Figure ١** shows the XRD patterns of the sodic and the pillared bentonite obtained.

The XRD analyses show in all cases, a clear shift of the signal at 13.22 Å (corresponding to the smectitic signal for the sodic bentonite), to a value close to 19.44 Å, which represents an increase in the basal space of the pillared clay.
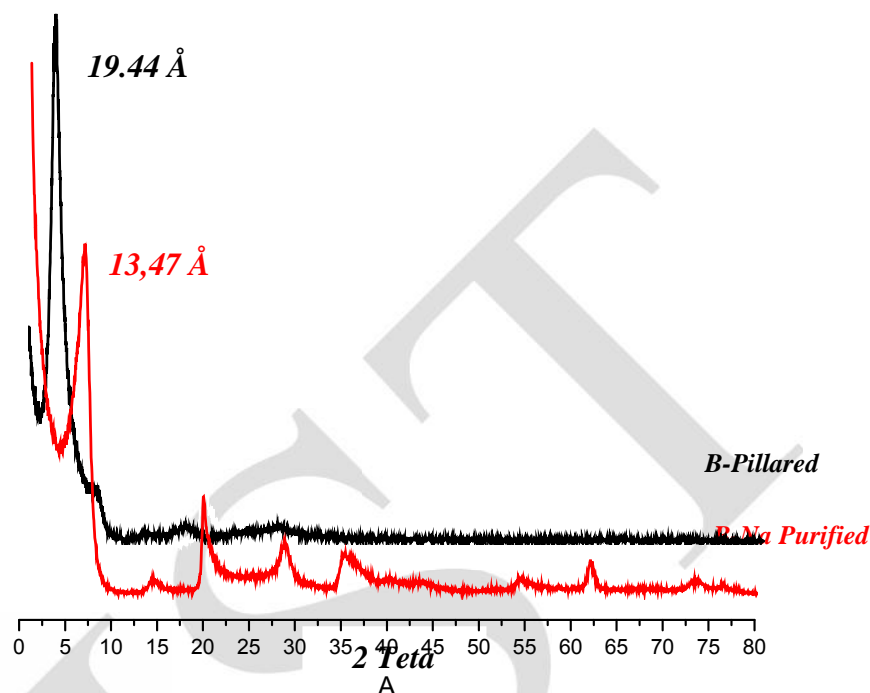

*Figure.*1*: X-ray diffractograms for the indicated samples*

This indicates that the chemical modification of the clays led to a successful pillaring process.

The basal spacing that expands to about 19.44 Å is equal to the thickness of one clay layer (9.4 Å) plus the height of one Al_{13} cation (9.7 Å) .

3.2.2   *Textural characteristics*

These analyses were done in order to determine the influence of chemical modification of clays (purified sodium and pillared bentonite) on there structural characteristics. Before analyses the samples were automatically degassed under vacuum for 4 h at 475 °K; the samples mass used are 0.1318 g and 0.1438 g of purified sodium and pillared bentonite.
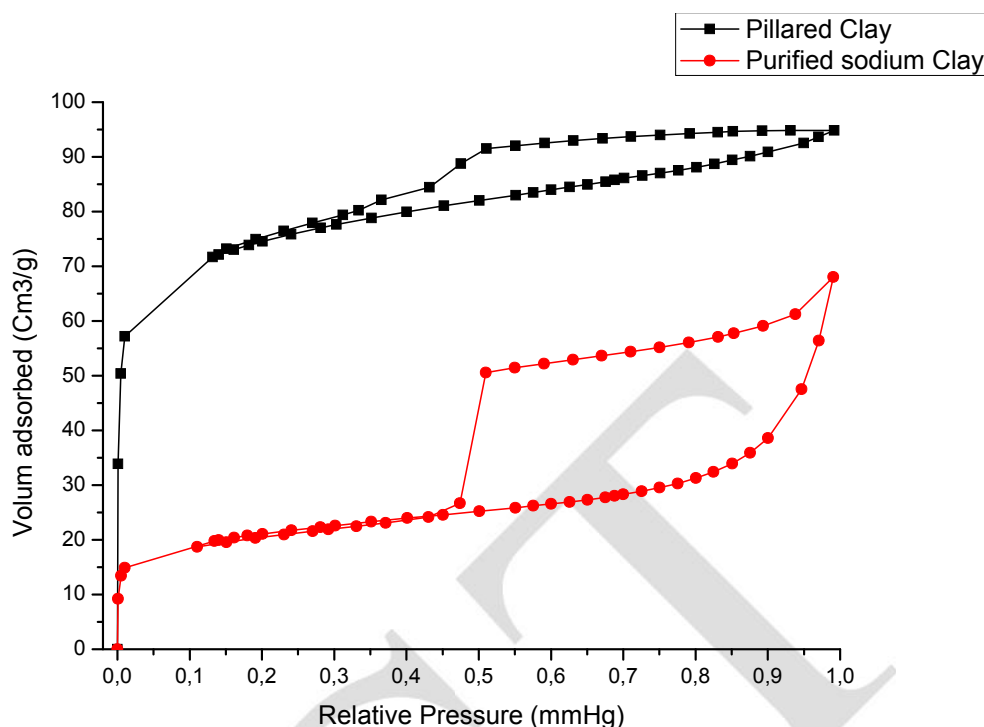
Figure.٢: Nitrogen adsorption-desorption isotherm for Pillared & purified sodium bentonite

The adsorption-desorption isotherms are important due to the parameters that can be established: specific surface area, porosity, pore volume, pore size distribution and average pore diameter. More, we can also obtain qualitative information regarding the structure (pores shape, interconexions etc.). To determine the textural characteristics several models are proposed[6].

In order to determine the textural properties[9], the Langmuir model in a range of relative pressure smaller than 0.07, and the correction to the BET model proposed by (Remy et al.1996)[10] were used. The microporous areas were determined by curves using the De Boer's method, and the micropore volumes were determined by curves using the Harkin-Jura equation.

The adsorption-desorption isotherms with N_2 of purified sodium bentonite (B-Na purified) and the pillared bentonite (B-Al-PILCs) , are shown in **Figures ٢**. The comparison between the tow isotherms , lead to a type IV isotherm with H1 hysteresis for B-Na purified[11] and H3 hysteresis for B-Al-PILCs[11]. This means that in the case of sodium purified bentonite (B-Na), the distribution of pore size is regular, and the increase in the adsorption of N_2 for B-Al-PILCs in comparison to the B-Na purified, as a result of the porosity generated because of the pillaring process.

The pillared material present developed mesoporosity and the hysteresis has a narrow loop with two branches which are almost vertical and parallel.This form of hysteresis is often associated with adsorbents made up of agglomerates and aggregated plane particles forming slit shape and narrow size pore distribution. Relevant data for the sodic purified and pillared bentonite obtained are presented in **Table I.**

Table III. Selected textural properties of the investigated samples.

Samples	S_{BET} (m²/g)	S_{ext} (m²/g)	$V_{0,991}$ (cm³/g)	V_{mic} (cm³/g)	D_{max} (Å)	D_{med} (Å)
B-Na Purified	107.5	81.024	0.123	0.053	14.547	5.32
B-AL-PILL	270.430	83.68	0.246	0.078	17.963	8.9

S_{BET}: specific surface area; $V_{0,98}$: Total pore volume; V_{mic} : Micropore volume; D_{max} : The pore diameter where the maximum of derivative cumulative volume curves is reached; D_{med} : Median value of pore diameter.

The increase in the superficial area and the porous volumes of the B-AL-PILCs compared to B-Na purified is remarkable[12]. This increase could be related to the high introduction of Al in the clays, and the high homogeneity and intensity of the pillaring signals reached by the methodology used in this paper. The superficial area of the B-AL-PILCs is determined mainly by the microporous area **Table II,** which is evident for of a significant textural modification of the B-Na purified.

3.2.3   *FTIR spectroscopy*

FTIR spectra of B-Na purified and B-Al-PILCs clays are given in **Figures ٣ and ٤**. At high frequency regions of the infrared spectra **Figure. ٣,** bands corresponding to the water molecules present in the interlayers and the structural hydroxyl groups in the clay layers were observed in the region between **3350-4000** cm^{-1}. The absorption band at **3450** cm^{-1}, corresponds to the symmetric O–H stretching vibration of H-bonded water, **Figure ٣**.
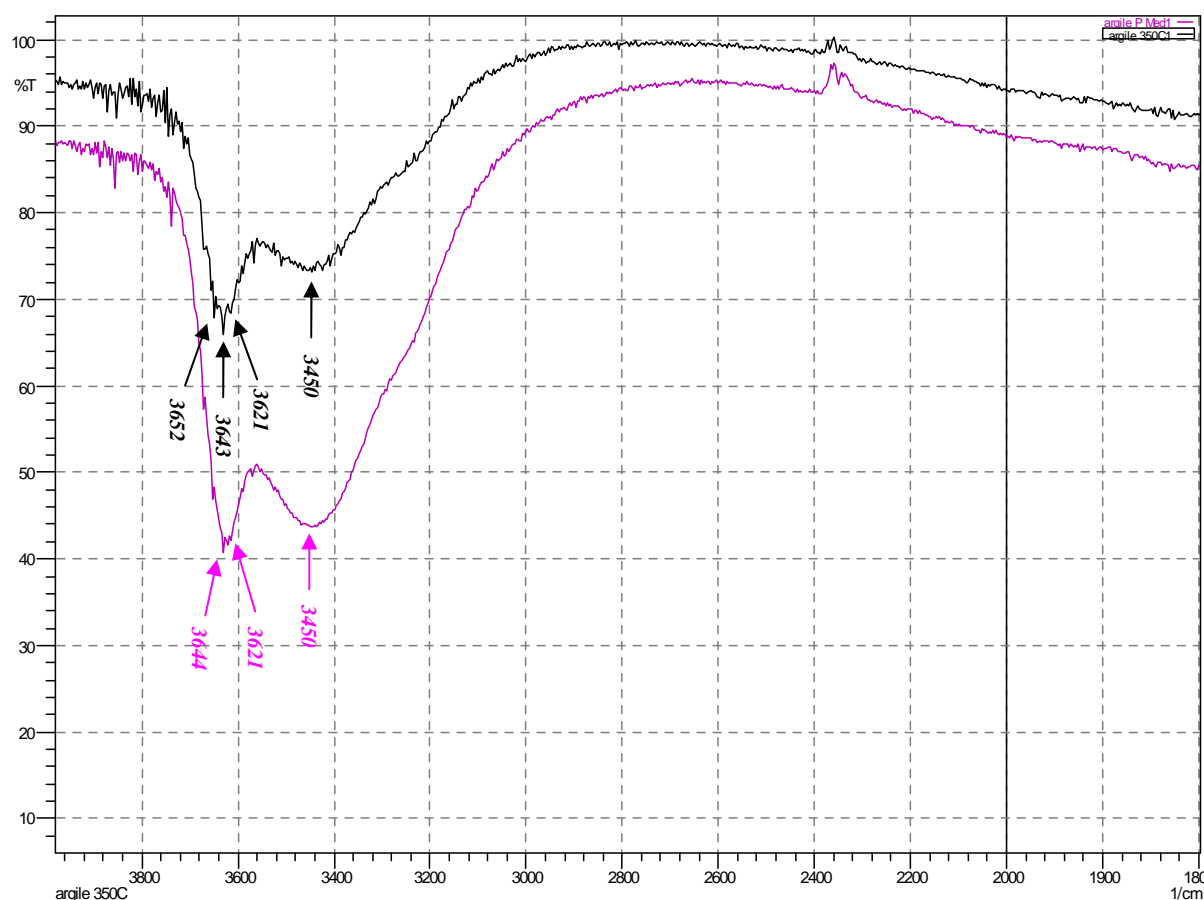
Figure.٣: FTIR spectra of B-Na purified and pillared in the range of 4000-1800 cm⁻¹

Also, it can be seen that its intensity is dependent on the type and the concentration of the interlayer cations. For B-Al-PILCs, the band locates at **3643** cm^{-1} and the intensity is higher than that of B-Na purified **3644** cm^{-1}. The former is ascribed to the O–H stretching vibration in hydroxy-Al cations while the latter corresponds to the hydroxyl groups involved in water–water hydrogen bands[13]. The samples show a band at **3621** cm^{-1} related to the OH stretching of Si-OH, corresponding to silanol groups. Such hydroxyls are either located at corners and fractures of sheets or are formed by the processes of tetrahedral inversion. For B-Al-PILCs sample, a new band is found at **3652** cm^{-1} **Figure ٣**, which is probably produced by the change of position of the SiOH group in the structure of the smectite. The original position was altered by the entrance of the Al ion in the smectite structure, which is likely to be due to Si-OH species perturbed by pillars, and designated as SiOH*.
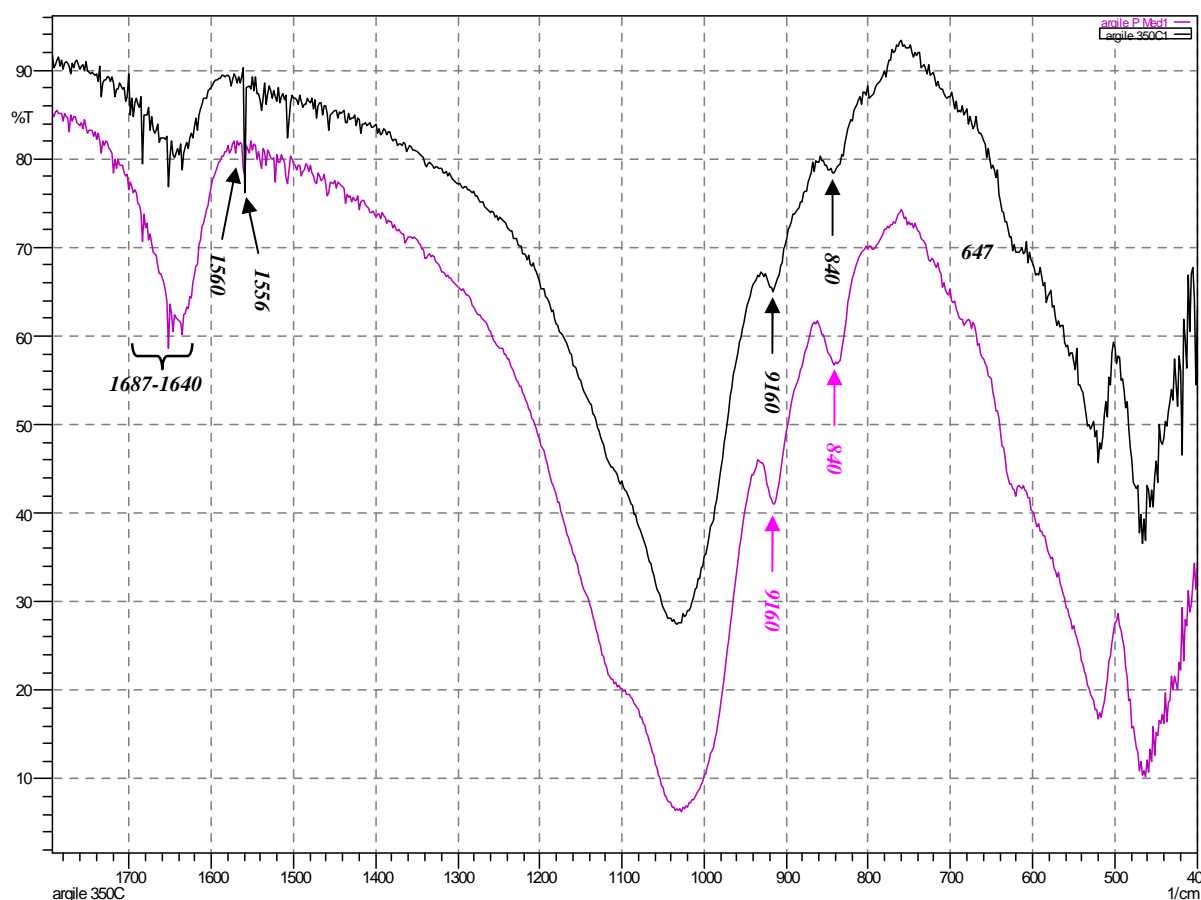
Figure. ٤: FTIR spectra of B-Na purified and B-Al-PILCs in the range of 1800-400 cm^{-1}

The low frequency regions of the infrared spectra of the B-Na purified and B-Al-PILCs are very similar, but the latter shows a very small low intensity band at **550-450** cm^{-1} originated from Si-O bending and Al-O stretching vibration and there were no changes in Si-O bending, but a small increase in Al-O stretching in intensity by pillaring. This situation was supported by the increase in Al content of pillared samples around **657** cm^{-1} **Figure ٤**. The lattice vibration at **657** cm^{-1} can be ascribed to the Al–O bond of tetrahedrally coordinated Al cations in the center of the Al_{13} pillars[14]. The band center of B-Al-PILCs locates at **1556** cm^{-1} with a higher intensity compared with that of B-Na purified at **1560** cm^{-1}. This should be attributed to an increase of water content in B-Al-PILCs, resulted from the intercalation of hydroxy-Al cations into the clay interlayer space. The infrared spectra of B-Na purified presented bands in the region of **1687–1640** cm^{-1} attributed to hydrating water. The aluminum pillaring agent had caused a decrease in the free silica peak intensity which occurred at **840** and **916** cm^{-1}.

3.2.4   Thermal analysis (DTA-TG)

The thermal curves are depicted in **Figures. ٥ and ٦** in the 30–1000°C range. The curves correspond to the starting purified sodium and pillared bentonite, after equilibrating in a desiccator, at room temperature. The general feature of thermal curves clearly reveals two steps: (1) in the 30–340°C and (2) in the 300–650°C temperature ranges.

The first step with purified sodium and pillared clay has been ascribed to physisorption of the hydrating water, whereas the second step is due to dehydroxylation of silicate structure.
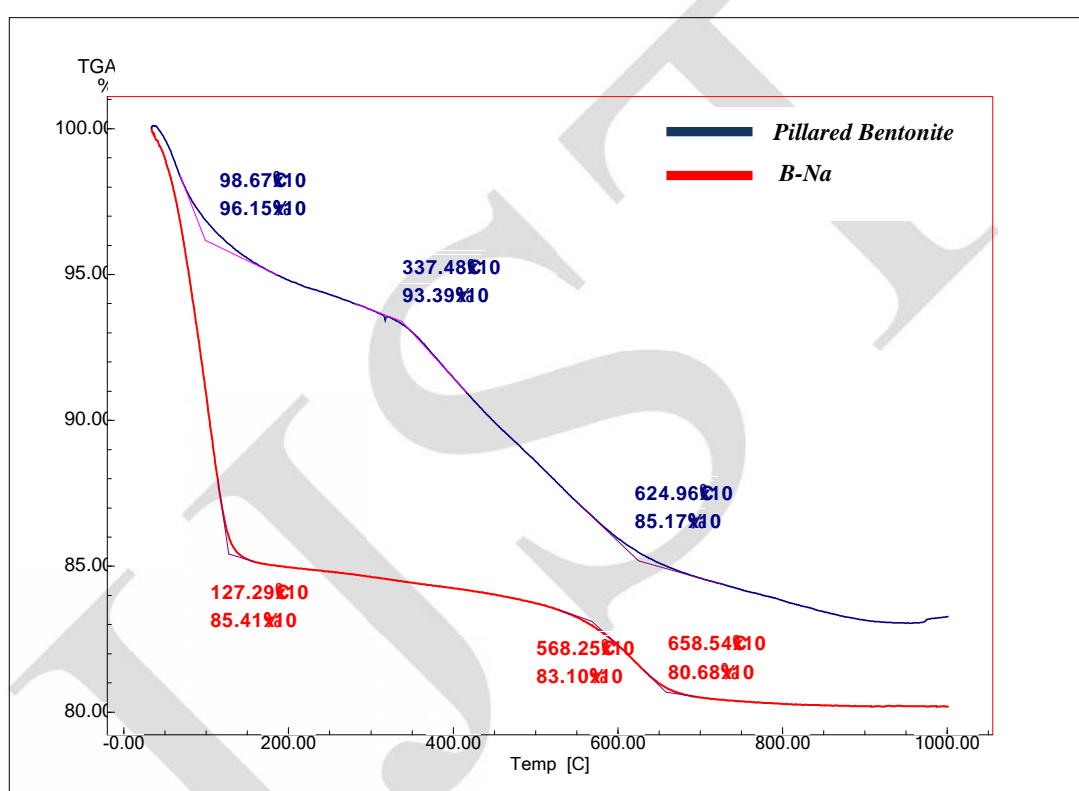

Figure.   : TG analysis of the pillared and purified sodium bentonite

Sometimes, this step occurs dissociated into two which is not well visible here but is clearly shown in the corresponding DTG and, moreover, in the TGA curve **(Figure. ٥)**, denoting dehydroxylation of the silicate structure in two different environments. For Al pillared materials, the net isomorphic substitution in the clay with different bonding strengths between the oligocations and the surrounding oxygen (or hydroxyl) ions can be observed[15]. Dehydroxylation continues between 337 and 650°C and is also detected to approximately 620 °C in an important step. This step is related with the stability of the pillars, since an important decrease in the basal spacing values occurs at this temperature,

indicating the collapse of the clay structure. Therefore, the thermogravimetric analyses are in agreement with the aforementioned thermal stability of the synthesized pillared clay up to 650°C.
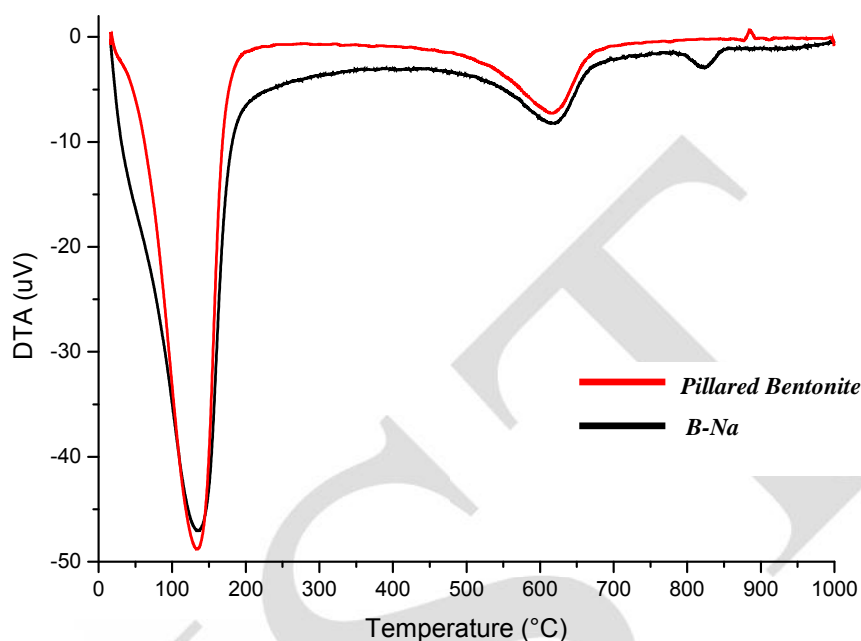

Figure.٦: DTG curves of the pillared & purified sodium bentonite

3.3. Adsorption isotherms

Adsorption isotherms and Amount of Lavandula angustifolia components are shown in **Figure ٨ & ٩**, Adsorption decreased in the order:

Cuminic Aldehyde > Verbenone > 2-beta pinene > M-Cymene > 14-Norcadin-5-En-4-One Isomer B > Limonene > 1,8 Cineole > Beta Eudesmol. And all the rest of compounds show a total adsorption on pillared bentonite.

The adsorption isotherms also show the existence of an over saturation for: 1-8 Cineol, and M-Cymene which have the highest concentrations or which is due to the saturation of active sites of the support surface like
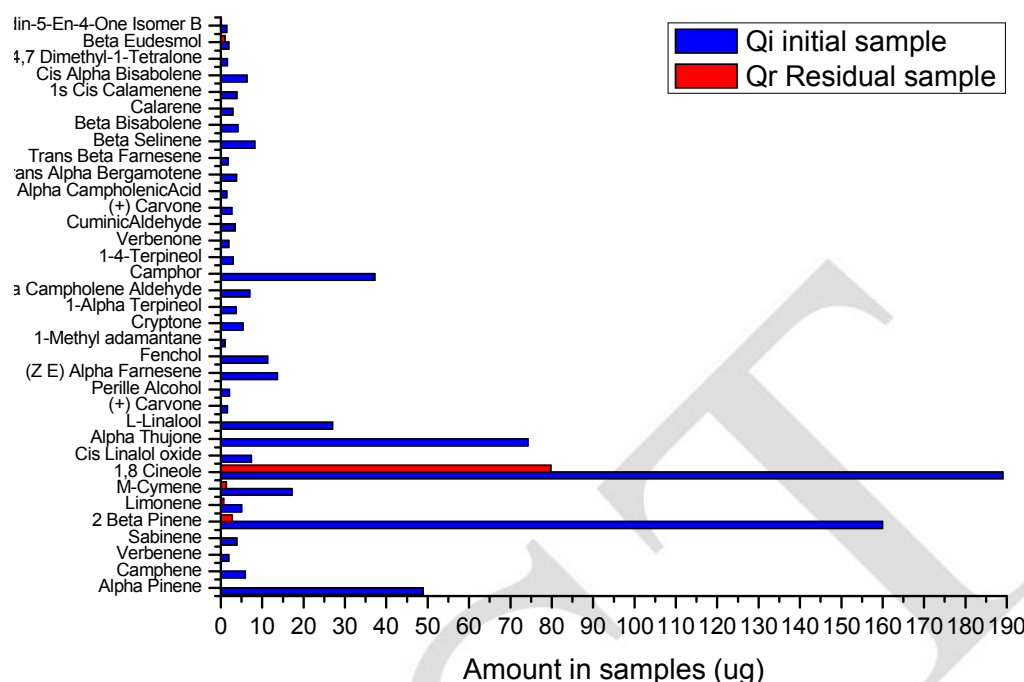
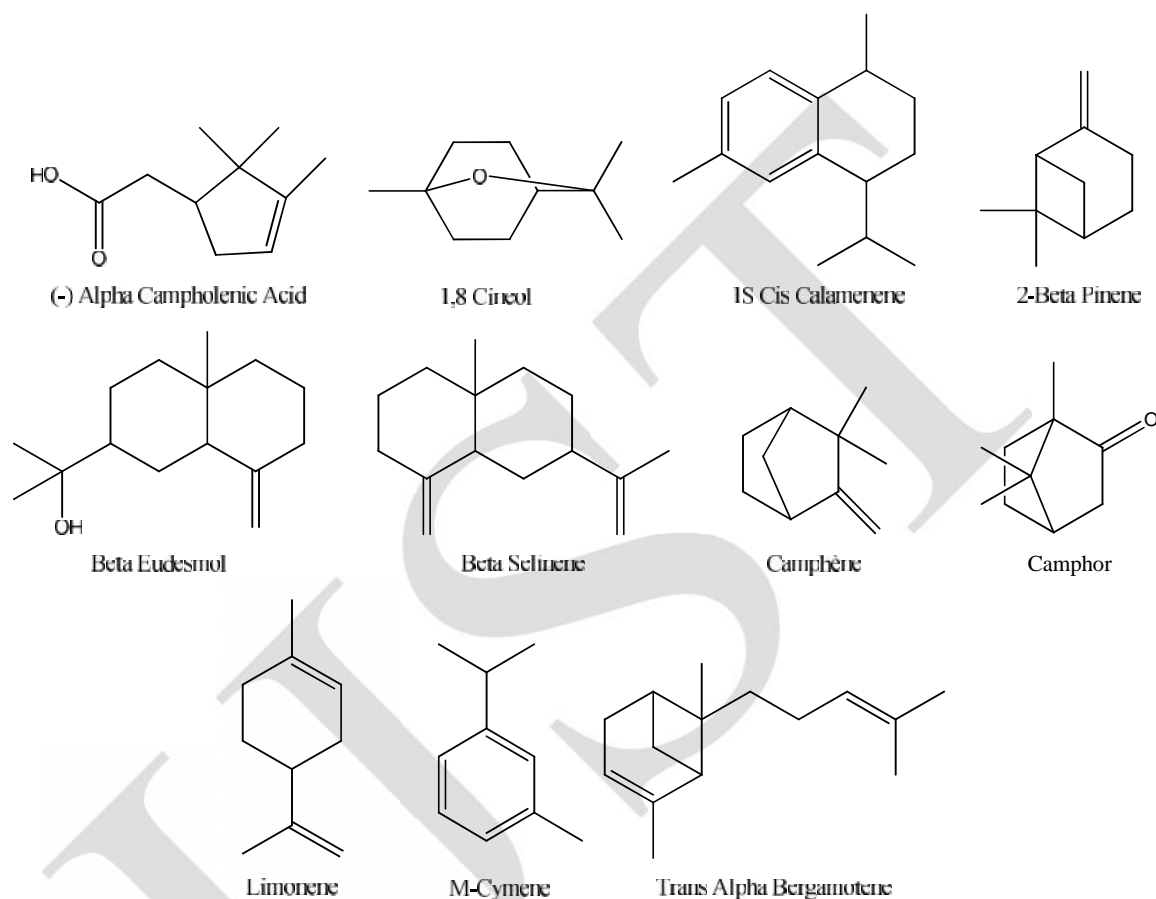**Figures. Ⅴ. the Amount of each compound in initial and residual sample**

The same phenomenon is observed for (-) -Campholenic acid and   -Eudesmo, the over saturation of the last tow is due to the saturation of all active sites by other most concentrated components as the 2-bêta pinene, 1-8 Cineol…..This shows that their adsorption affinity for pillared bentonitr is low, compared to the other compounds that are totally adsorbed.

comparing these results with the results of M. Elmiz, et al 2014 (Adsorption of essential oil components of Lavandula Angustifolia on sodium modified bentonite)[5] shows that verbenene, Limonene, M-cymene, Beta bisabolene, Cis Calarene and   bisabolene, have no affinity for the bentonite; whilst their adsorption is very low in sodium bentonite purified while a total adsorption is observed for pillared bentonite, is also observed that more than 96 % of essetiel oil compounds were completely adsorbed on pillared bentonite whereas, only 82% of the compounds have been adsorbed on sodium bentonite[5].
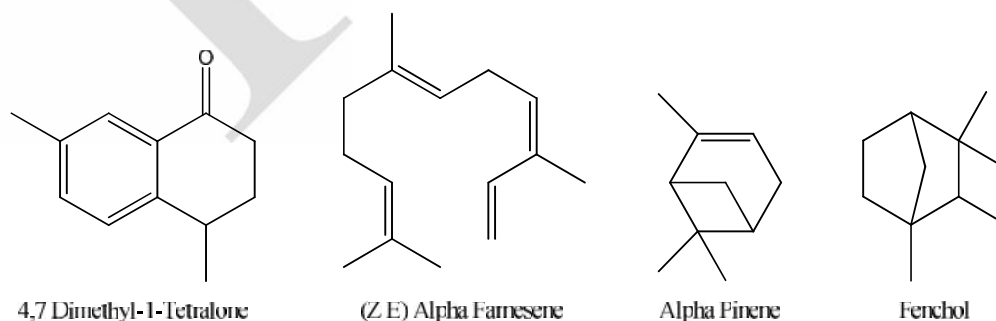
This adsorption amount of terpenics and the other components could be a result of many factors. The selectivity was affected by the abundance of each component in the crude essential oil: 2-beta pinene, Alpha thujon, Camphor, L-linalool, Fenchol, (Z E) alpha farnesene; these were the most adsorbed compounds as they were the most abundant ones.
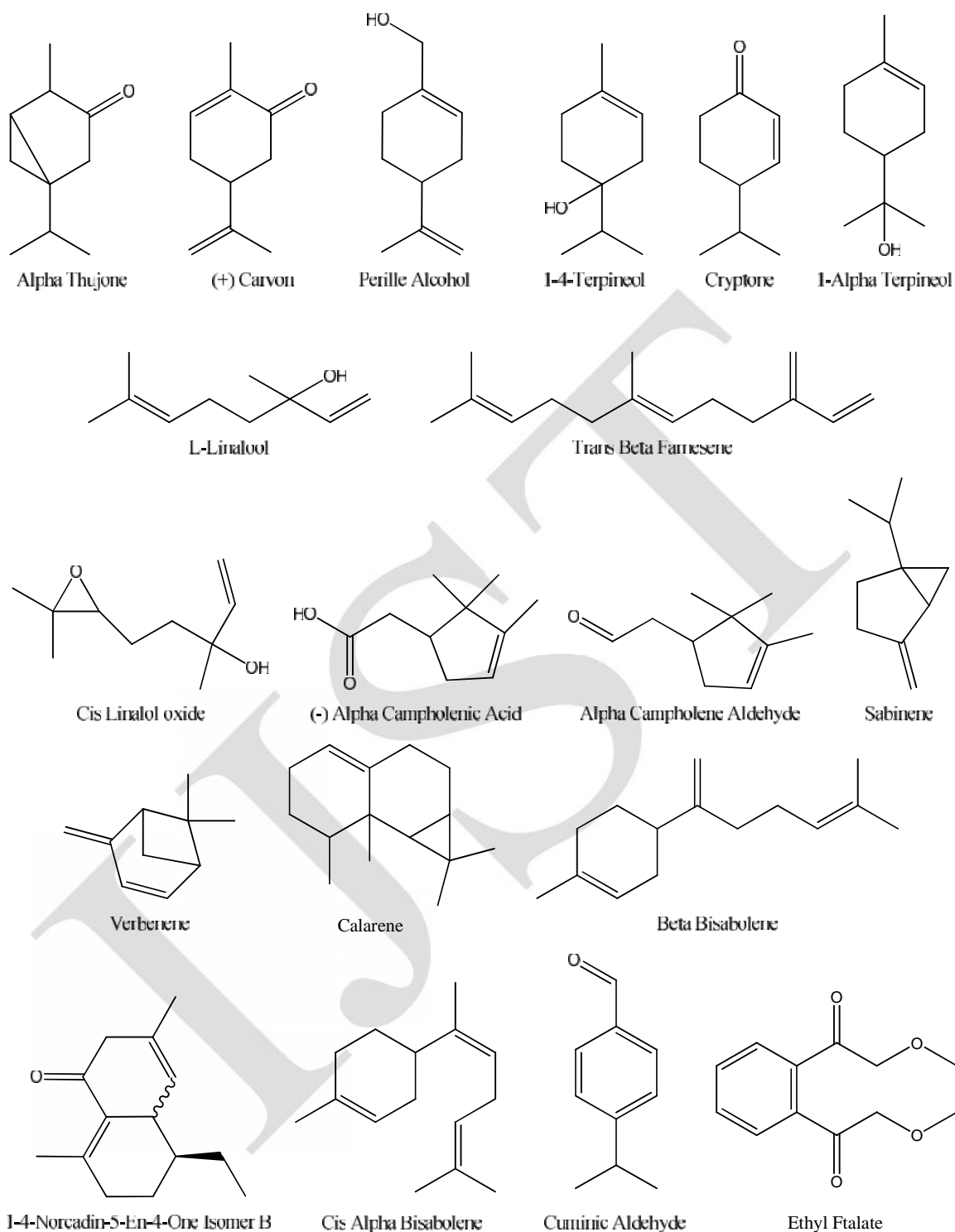
The selectivity of adsorption was affected by the polarity of terpenic components: 2-beta pinene 1-8 cineol and alpha thujon were adsorbed in larger amounts than some others mono-terpene hydrocarbons. We also note that the charge neutrality of the surface of pillared bentonite promotes the creation of hydrogen and Van deer Walls interactions between the support and the compounds.

- **Major components in Lavandula angustifolia essential oil with adsorption isotherms:**

(-) Alpha Campholenic Acid   1,8 Cineol   1S Cis Calamenene   2-Beta Pinene

Beta Eudesmol   Beta Selinene   Camphène   Camphor

Limonene   M-Cymene   Trans Alpha Bergamotene

- **Major components in Lavandula angustifolia essential oil with total adsorption:**

4,7 Dimethyl-1-Tetralone   (Z E) Alpha Farnesene   Alpha Pinene   Fenchol

Alpha Thujone   (+) Carvon   Perille Alcohol   1-4-Terpineol   Cryptone   1-Alpha Terpineol

L-Linalool   Trans Beta Farnesene

Cis Linalol oxide   (-) Alpha Campholenic Acid   Alpha Campholene Aldehyde   Sabinene

Verbenene   Calarene   Beta Bisabolene

1-4-Norcadin-5-En-4-One Isomer B   Cis Alpha Bisabolene   Cuminic Aldehyde   Ethyl Ftalate

3.4.   Equilibrium modeling

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state.

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. There are several isotherm equations available for analyzing experimental adsorption equilibrium data.

Three isotherms were tested for their ability to describe the experimental results, namely the Langmuir isotherm, the Freundlich isotherm.

3.5.   Langmuir & Freundlich models

Under ideal saturated conditions, the solid liquid ratio should not influence the amount of organic or inorganic molecules adsorbed per unit of adsorbent. However, some interested studies have[16] shown that both organic and inorganic contaminant adsorption is dependent on solid-liquid ratio to some degree and the competition system of mixture.

In order to optimize the design of an adsorption system and to optimize the use of capsules in various formulations, it is important to establish the most appropriate correlation for the equilibrium curves.

In this respect, the equilibrium experimental data of the adsorption of each component in the crude essential oil on clays were studied using Freundlich and Langmuir models.

The Freundlich model Van Bemmelen and Freundlich is an empirical equation employed to describe heterogeneous systems; characterized by the heterogeneity factor nf, describes reversible adsorption, and is not restricted to the formation of the monolayer[17].

- **The Langmuir isotherm model:**

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the sorbed molecules.

The linear expression of the Langmuir model is given by **Eq 5.**

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_m} + \left(\frac{1}{q_m}\right) \times C_e \qquad \textbf{eq : 6}$$

The Langmuir constants q_m and K_L were determined from the slope and intercept of the plot and are presented in **Table IV**.

- **The Freundlich isotherm model**

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The linear form of Freundlich equation is expressed:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \times \ln C_e \qquad \textbf{eq : 7}$$

Where K_F and n are Freundlich constants with K_F (mg/g (L/mg), (1/n) is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the exponent, 1/n, gives an indication of the favorability of adsorption.

The Value of K_F and n are calculated from the intercept and slope of the plot and listed in **Table IV**.

The plot of amount adsorbed (Ln qe) against the equilibrium concentration (Ln Ce) shows that the adsorption obeys the Freundlich model[17, 18].

Table: IV. Langmuir and Freundlich adsorption constants of Lavandula angustifolia oil on sodium modified bentonite

The Langmiur isotherm model						
Compounds	**R^2**		**Value**	**Stand Err**	**K_L**	**qm_{Theor}**
1 Cis Calamenene	**0.99395**	*Intercept*	0,0130	0.00411	9.952	7.694
		Slope	0.1299	0.00359		
2 –β pinene	**0.98416**	*Intercept*	0.0061	0.00224	6.226	26.116
		Slope	0.0382	0.00183		
(-) α Campholenic Acid	**0.77719**	*Intercept*	0.0092	0.00636	11.441	9.439
		Slope	0.1059	0.02101		
β Selinene	**0.99831**	*Intercept*	0.0010	5.616 E^{-4}	18.210	52.301
		Slope	0.0191	3.209 E^{-4}		
Limonene	**0.99272**	*Intercept*	0.0035	0.00181	11.317	25.031
		Slope	0.0399	0.0014		
β Eudesmol	**0.48422**	*Intercept*	0.0113	0.00772	5.086	17.262
		Slope	0.0579	0.02249		
Camphene	**0.93555**	*Intercept*	0.0144	0.00349	1.502	46.125
		Slope	0.0216	0.00214		
Camphor	**0.9822**	*Intercept*	3.575 E^{-4}	9.387 E^{-5}	3.692	757.575
		Slope	0.0013	5.897 E^{-5}		
Trans α Bergamotene	**0.88391**	*Intercept*	0.0032	0.00101	5.069	61.652
		Slope	0.0162	0.00237		
1.8 Cineol	**0.09614**	*Intercept*	0.0130	0.00411	9.952	7.694
		Slope	0.1299	0.00359		
M-Cymene	**0.44611**	*Intercept*	0.0061	0.00224	6.226	26.116
		Slope	0.0382	0.00183		
The Freundlich isotherm model						
Compounds	**R^2**		**Value**	**Stand Err**	**K_F**	**n**

1 Cis Calamenene	**0.89715**	*Intercept*	1.92347	0.02501	6.8447	4.2431
		Slope	0.23566	0.03528		
2 –β pinene	**0.73366**	*Intercept*	3.10097	0.12149	22.2195	2.3923
		Slope	0.418	0.12058		
(-) α Campholenic Acid	**0.69451**	*Intercept*	2.23314	0.19099	9.3291	3.0158
		Slope	0.33158	0.10437		
β Selinene	**0.99159**	*Intercept*	3.92045	0.01088	50.4231	3.8405
		Slope	0.26038	0.01383		
Limonene	**0.90385**	*Intercept*	3.08993	0.01664	21.9755	6.8217
		Slope	0.14659	0.02713		
β Eudesmol	**0.7912**	*Intercept*	2.73848	0.27384	15.4635	1.8422
		Slope	0.5428	0.15435		
Camphene	**0.95995**	*Intercept*	3.39709	0.0138	29.8770	2.7311
		Slope	0.36614	0.0372		
Camphor	**0.94336**	*Intercept*	8.50469	0.3464	4937.8732	0.5781
		Slope	1.72977	0.21035		
Trans α Bergamotene	**0.92908**	*Intercept*	4.09704	0.15159	60.1619	1.9389
		Slope	0.51574	0.08124		
1.8 Cineol	**0.80673**	*Intercept*	3.97338	0.48121	53.1639	1.5520
		Slope	0.64432	0.13777		
M-Cymene	**0.91988**	*Intercept*	-7.19533	1.23429	0.0008	0.6287
		Slope	1.59051	0.26716		

The plot of Ln qe vs. Ln Ce according to the Freundlich model and correlation coefficients (R^2) indicates that adsorption isotherm is linear for: 1-8 Cineol, Beta, Beta eudesmol, camphene, Trans alpha Bergamotene, M-Cymene. But the sorption behaviour of others compounds does not conform to this model.

The Langmuir model was also fit for describing the sorption behaviour of Lavandula angustifolia essential oil. The coefficients (R^2) for Langmuir model shows that the sorption of: 1-Cis Calamenene, 2–Beta pinene, (-) Campholenic Acid, Camphor, Beta Selinene, Limonene, can conform to the Langmuir model.

Considering some individual components, they presented the highest adsorption capacity:

Camphor with qm = 529.943 ug/g et K_L = 3.692, K_F =4937.873 and n = 0.5781 puis 1-8 Cineol with qm = 644.86 ug/g, K_L = 0.541, K_F = 9.952 and n = 1.5520.

We also note that the values of $qm_{(exp)}$ are compatible with the values of $qm_{(theo)}$ especially for compounds that follow the Langmuir model as:

1-Cis Calamenene (qm_{theo}= 7,694 ug/g and qm_{exp} = 7.266 ug/g), 2–Beta pinene (qm_{theo}= 26,116 ug/g and qm_{exp} = 24.546 ug/g), (-) Campholenic Acid (qm_{theo}= 9.439 ug/g and qm_{exp} = 6.18 ug/g),

Camphor (qm$_{theo}$= 757.575 ug/g and qm $_{exp}$= 529.943 ug/g), Beta Selinene (qm$_{theo}$= 52.301 ug/g and qm$_{exp}$ = 51.81 ug/g), Limonene (qm$_{theo}$= 25.031 ug/g and qm$_{exp}$ = 23.75 g/g).
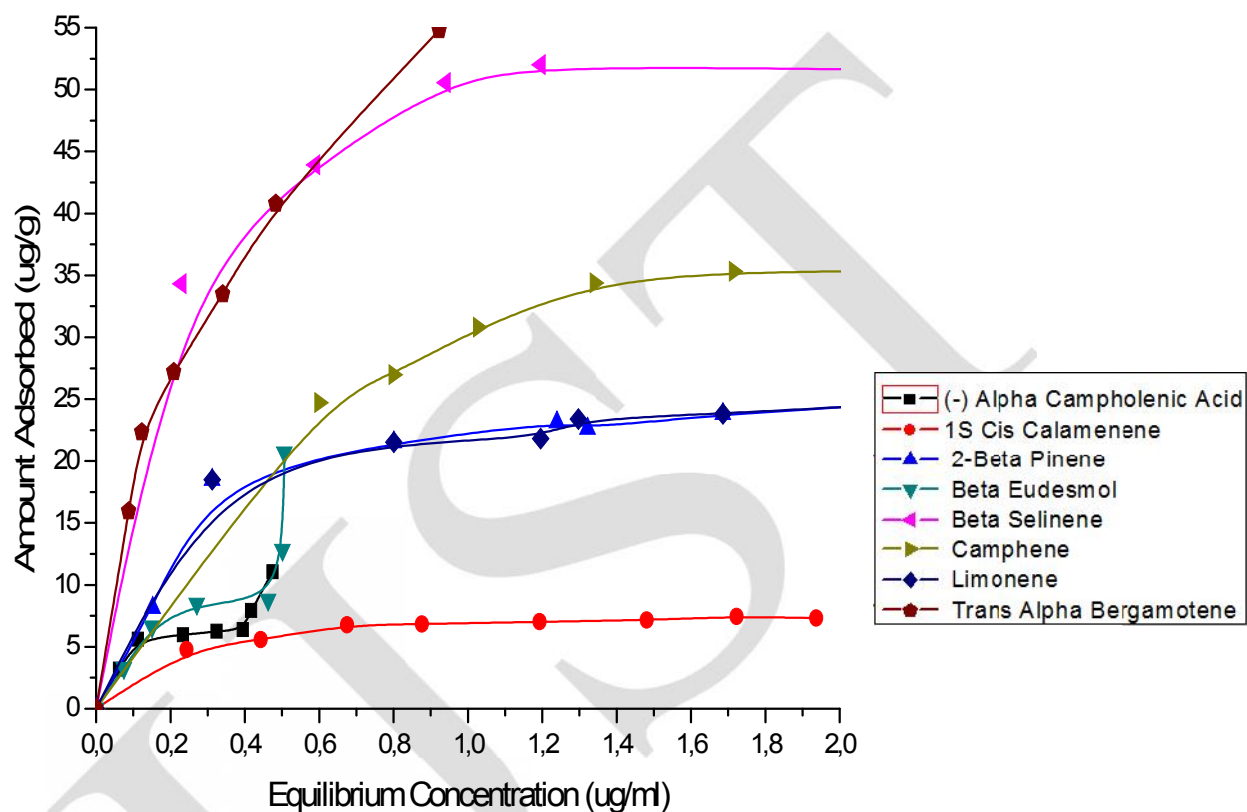

Figure.ᴧ. Adsorption isotherms of Lavandula angustifolia components on Pillared bentonite
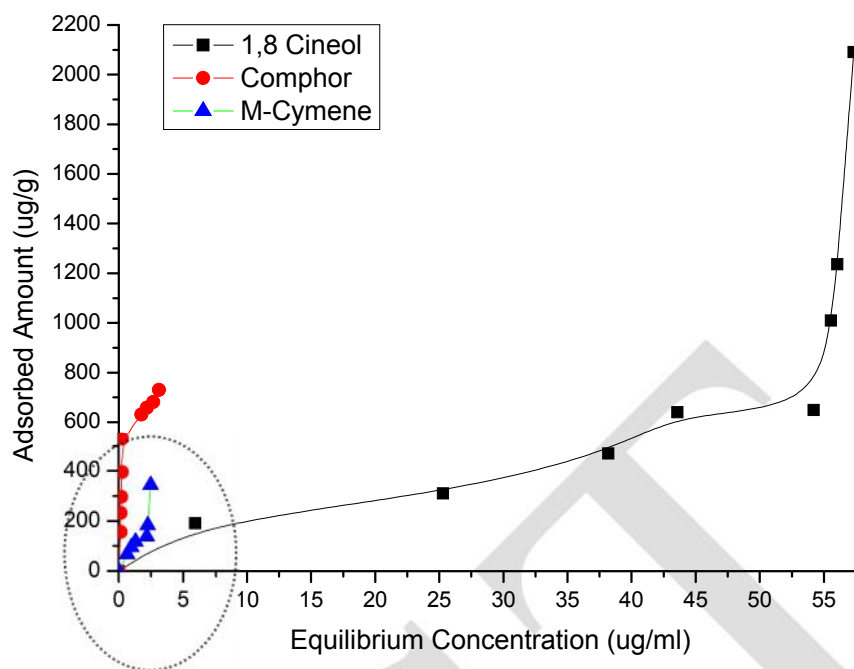
Fig.٩. Adsorption isotherms of Lavandula angustifolia Majors components on pillared
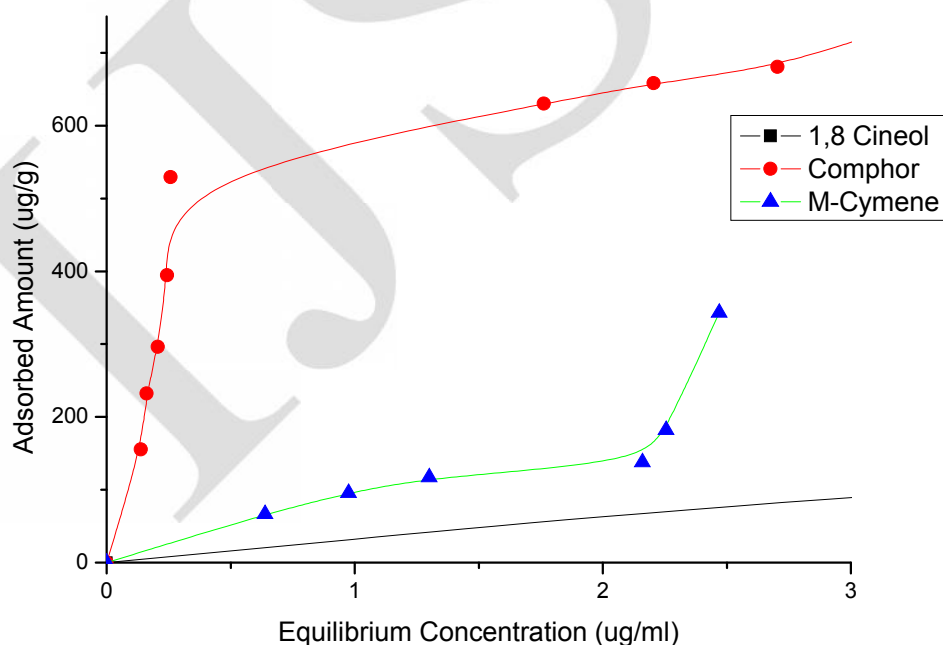
Bentonite:

Figure.   . Adsorption isotherms of Lavandula angustifolia Majors components on Pillared bentonite (Zoom 1):

4. Conclusion:

The terpenes: 1,8 Cineol, Camphor, M-Cymene was adsorbed by Pillared bentonite in higher amounts than others compounds.

The adsorption amount of terpenics and the other components was a result of many factors. The selectivity was affected by the abundance of each component in the crude essential oil, the particle size fractions; (the finer fractions adsorbed higher amounts) and the polarity of each components (Chomphor, 1-8 cineol and M-Cymene) were adsorbed in larger amounts than some other. The adsorption isotherms was fitted with the Langmuir like: 1-Cis Calamenene, 2–Beta pinene, (-) Campholenic Acid, Camphor, Beta Selinene, Limonene and Freundlich model like: 1,8 Cineol, Beta eudesmol, camphene, Trans alpha Bergamotene, M-Cymene.

It was also observed that more than 96 % of essetiel oil compounds were completely adsorbed on pillared bentonite whereas; only 82% of the compounds have been adsorbed on sodium bentonite[5]. These results show that pillared bentonite can be used to encapsulate essential oils (preparation of essential oil-powder formulation).

5. Acknowledgements

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