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Full Length Research Paper

Adsorption of essential oil components of *Lavandula* angustifolia on sodium modified bentonite from Nador (North-East Morocco)

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The analysis of essential oil has basically one technical goal: to achieve the best possible separation performance by using the most effective, available and current technology of chromatography. The present work aimed to study 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 *L. angustifolia*; they were extracted by hydro distillation and were analyzed by gas chromatography-mass spectrometry (GC-MS) and gas chromatography flame ionization detector (GC-FID). 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 GC-FID. The identified components accounted for more than 95% for each essential oil. The results of these studies show 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.

INTRODUCTION

Clays are widely used in pesticide formulation as adsorbents or particulate fillers. Many researchers studied the adsorption of pesticide on clay material (Lagaly, 2001) to limit pest damages. Therefore, the common method used to prevent stored products from insect attacks is the one that make use of synthetic insecticides. The use of such insecticides is increasing year after year. It is evident that the intensive and

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Author(s) agree that this article remain permanently open access under the terms of the <u>Creative Commons Attribution License 4.0</u> International License uncontrolled use of chemical insecticides has direct effect on consumers and on the environment. Therefore, there is a need to develop environment friendly products that present less dangerous effect on both the environment and the consumer.

Essential oils of aromatic plants currently used are considered to be a good tool to prevent insect attacks on stored grains (Ngamo et al., 2007). The most important difficulty to popularise this new tool is to produce a new formulation of a chemical active insecticide with moderate persistence (Lajide et al., 1995; Keita et al., 2001). Due to 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 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.

Clays, used in different fields of application such as ceramics, paper, paint, barrier, adsorbent, catalyst are among the most important industrial raw materials (Grim and Güven, 1978; Murray, 2000; Bergaya and Vayer, 2006). These clays are composed of minerals belonging generally to the clay stone groups. They are used either in the natural state or treated by various methods to improve some of their characteristics.

This paper presents the study of the adsorption of active components of *Lavandula angustifolia* essential oil on sodium purified bentonite. *L. 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*, *L. angustifolia*, *Lavandula latifolia*, *Lavan-dula intermedia*, *Lavandula stoechas* and *Lavandula dhofarensis* (Hanamanthagouda et al., 2010). 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 (Muyima et al., 2002). 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 (Cavanagh and Wilkinson, 2005).

Lavandula essential oils are obtained from the flowering tips of the plants *L. angustifolia* (lavender). These essential oils have a popular and easily recognisable fragrance. Pure *L. angustifolia* essential oils are used in aromatherapy, and are thought to have calmative, anti-flatulence, and anti-colic properties (Lis-Balchin and Hart, 1999).

Lavandula essential oil contains various components depending on the species, but there is usually linalyl

acetate and linalool, geraniol, pinene, cineol, coumarin and ethylamyl-cetone (behind its refreshing scent). Lavender essential oil used in this study is the *angustifolia* type, from Al Hoceima (North region of Morocco).

MATERIALS AND METHODS

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 gas chromatography-mass spectrometry (GC-MS).

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.

Preparation of the sodium modified bentonite

The clay samples used for these analyses were collected from Nador (North-East Morocco, North Africa). The bentonite was purified and modified by sodium before it was used. Adsorption isotherms which represent the adsorbed amount versus the equilibrium concentration have been identified for each compound.

Natural clay from North-East Morocco (Nador), was used in a purified form. The clay is an industrial bentonite rich with bentonite clay type. Purification was done by removing all the crystalline phases (quartz, feldspar, calcite, ...), by a preliminary treatment of the raw sample by ionization homo-sodium, and it began first with a series of washings to remove impurities and thereby have a granular fraction of a well defined size ≤ 2 microns. The sodium modified clay are subjected to analysis and identification by X-ray diffraction (XRD), infrared spectroscopy (IR) and textural characteristics.

X-ray diffractograms were recorded in a Shimadzu XRD diffractometer D6000 stations working on the monochromatic copper K α 1 radiation (1.54 Å) (Figure 1). Infra red (IR) spectra were acquired using a Shimadzu Fourier Transform spectrometer over a range 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) (Figure 2).

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 Table 1. Identification results of the components and the percentage of each compound in essential oil.

Product name	QI	Rt	Surface	C _x (µg/ml)	KI	% in samples
Alpha Pinene	95	10.09	282.35	24.43	942	6.05
Camphene	97	10.40	33.98	2.940	957	0.72
Verbenene	96	10.52	10.88	0.94	963	0.23
Sabinene	81	10.92	22.11	1.91	982	0.47
2-Beta Pinene	97	10.98	924.1	79.96	985	19.81
Limonene	99	11.89	29.03	2.51	1033	0.62
M-Cymene	87	11.97	99.10	8.57	1038	2.12
1,8 Cineole	97	12.03	1092.38	94.52	1041	23.42
Cis Linalol oxide	97	12.75	42.67	3.69	1082	0.91
Alpha Thujone	98	13.04	428.84	37.107	1097	9.19
L-Linalool	94	13.17	155.95	13.49	1105	3.34
(+) Carvone	95	13.25	9.156	0.79	1110	0.19
Perille Alcohol	83	13.35	11.85	1.02	1117	0.25
(Z E) Alpha Farnesene	94	13.46	79.02	6.83	1124	1.69
Fenchol	96	14.31	65.198	5.64	1157	1.39
1-Methyl adamantane	93	14.38	5.557	0.480	1183	0.11
Cryptone	96	14.47	30.81	2.66	1189	0.66
1-Alpha Terpineol	72	14.57	21.28	1.841	1195	0.45
Alpha Campholene Aldehyde	58	14.67	40.32	3.48	1201	0.86
Camphor	98	14.78	215.14	18.61	1209	4.61
1-4-Terpineol	98	14.99	17.09	1.478	1224	0.36
Verbenone	99	15.08	11.12	0.96	1230	0.23
CuminicAldehyde	97	15.42	19.82	1.715	1255	0.42
(+) Carvone	98	15.46	15.34	1.327	1258	0.32
(-) Alpha CampholenicAcid	98	15.58	7.99	0.69	1266	0.17
Trans Alpha Bergamotene	98	18.05	21.94	1.89	1397	0.47
Trans Beta Farnesene	95	18.68	9.96	0.86	1502	0.21
Beta Selinene	96	18.78	31.45	4.082	1509	1.01
Beta Bisabolene	96	18.93	15.68	2.03	1523	0.5
Calarene	92	19.07	11.02	1.43	1535	0.35
1s Cis Calamenene	92	19.18	14.86	1.92	1545	3.91
Cis Alpha Bisabolene	91	19.32	24.11	3.13	1556	6.25
4,7 Dimethyl-1-Tetralone	92	19.46	5.86	0.76	1568	0.104
Beta Eudesmol	94	20.71	7.29	0.94	1678	0.23
14-Norcadin-5-En-4-One Isomer B	93	21.16	5.44	0.707	1707	0.17

Rt retention time; KI, Kovats indices; QI, Quality index of identification by comparison with the spectra library; C_x, Concentration of each compound in samples.

30 and 1000°C under N₂ atmosphere (Figure 3).

The surface areas and the pore volumes of the samples were determined by micrometrics ASAP 2000 volumetric adsorption-desorption apparatus, using nitrogen as adsorbent (Zaitan et al., 2008). In this method, a mass of 1 kg of raw clay was dispersed in 5 L of distilled water with a solid/liquid ratio: 1/5. The mixture was stirred for an hour, until the homogenization full suspension, followed by treatment with HCl (0.5 M) to remove carbonate. The resulting mixture was washed by H_2O_2 (10%) to oxidize organic matter.

The resultant product was then washed extensively (six times) with NaCl 1 M and centrifuged to give saturated clays. The dark grey residue in the centrifuge tube was eliminated because it contained the fraction enriched in impurity (quartz, cristobalite,

feldspar ...).

The samples were then washed and dialyzed against distilled water until the conductivity in the dialysis bath was less than 2 μ S/cm. The granular fraction size \leq 2 μm were then obtained as bay accurate sedimentation. The air dried clays were gently grounded to give a powder.

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 and 0.206 g) were dispersed in 2 ml oil solution (0.754 mg of oil in 2 ml of solution) and equilibrated in an



Figure 1. Diffractograms of the fine fraction powder of raw and sodium modified bentonite.

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.

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

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

$$\%C = \frac{Cx}{Ceo} \times 100 \tag{4}$$

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:

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

Where, Veo is the volume of solution (ml).

RESULTS AND DISCUSSION

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. Chromatographic analysis showed that lavender essential oil contains more than 50

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:

$$\% adsorbed = \frac{100(A0 - Ax)}{A0} \tag{1}$$

Where, A_0 is the peak area of each oil component in the initial solution; A_x is 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).

$$C(\mu g/ml) = \frac{A0 \times As}{ms}$$
(2)

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

The amount of each compound adsorbed by clay fractions is:



Figure 2. Infra-red of raw and sodium modified bentonite.

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 (α -thujene, α -pinene, sabinene, β -pinene, limonene ...), oxygenated mono terpenes OM (Beta Eudesmol, Cis Linalol oxide, 1,8-cineole), sesquiterpene hydrocarbon ST, ((+) Carvone, Calarene, Cryptone, Verbenene).

Characterization of the bentonite

The major element composition of the investigated clay mineral is presented in Table 2 as % oxides. The main components are SiO₂ (61.17%) and Al₂O₃ (15.13%), with the exception of hectorite, which contains ~ 6% MgO, 4% CaO, Fe₂O₃ (3.25%) and other elements present in minor amounts (K₂O, SO₃, CuO, TiO₂ and ZnO). A small

percentage of organic matter (MO = 1.08%) and a percentage of water was estimated to ~ 10.56%.

The fine fraction ($\leq 2 \mu m$) was purified and sodium exchanged. The surface areas and the pore volumes of the samples: specific surface $S_{BET} = 83.5 \text{ m}^2\text{g}^{-1}$, total pore volume $V_t = 0.213 \text{ cm}^3\text{g}^{-1}$, External specific surface $S_{ext} = 81.024 \text{ m}^2\text{g}^{-1}$. Its cation exchange capacity, determined by adsorption of a copper ethylene di-amine complex (Amman, et al., 2005; Bergaya and Vayer, 1997), is 107 meq/100 g (ignited) clay. Chemical analyses of the samples are given in Table 1.

The samples of clays were characterized by X ray diffraction (XRD), differential thermal analysis and thermo gravimetric analysis (DTA-TGA) and infrared (I.R). XRD of the purified bentonite powder showed that the latter is of the same family of smectites with reflection (001) located at 12A. The presence of the line (06.33) at d = 1.49 Å showed that it consists of montmorillonite. The



Figure 3. TDA and TGA of sodium modified bentonite.

Table 2. Chemical composi	ition (wt %) of sodiu	um modified and raw bentonite
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Oxide	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O ₂	K₂O	SO₃	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

presence of crystalline phases in the form of impurities Quartz (Q) d = 3.34 Å was also noted.

XRD of Brute and purified bentonite powder shows that bentonite is of the same smectite family with reflection (001) at 14a. This shows that natural bentonite is a calcium form. The presence of the line (06.33) at d = 1.49 Å shows that it consists of montmorillonite. It is also noted that there is presence of crystalline phases in the form of impurities Quartz (Q) d = 3.34 Å. Examination of the infrared absorption spectra of the crude and purified samples of bentonite shows absorption bands that are presented as follows (Farmer, 1979; Salerno et al, 2001).

The spectra show two absorption bands between 3200 and 3800 cm⁻¹ and between 1600 and 1700 cm⁻¹. The tape that lies between 1600 and 1700 cm⁻¹ is attributed to stretching vibrations of the OH group constitution water plus the vibration binding adsorbed water. The band in the range 3200-3800 cm⁻¹ with a strong peak at the shoulders 3435 and 3621 cm⁻¹ characterize the montmorillonite and correspond to stretching vibrations of

the OH groups of the octahedral layer is coordinated with AI + Mg (3640 cm⁻¹) or AI 2 (3600 cm⁻¹).

The deformation vibrations of H_2O molecules are characterized by the band 3400 cm⁻¹. The band, centered around 1630 cm⁻¹, is assigned to the deformation vibrations of H_2O molecules adsorbed between the sheets.

The intense band situated between 900 and 1200 cm⁻¹ and centered around 1040 cm⁻¹ corresponds to stretching vibrations of Si-O bond. In the purified clay (Na-montm), it is situated around 1030 cm⁻¹ between 1115 and 1020 cm⁻¹. The bands situated at 425, 525 and 468 cm⁻¹ are assigned respectively to the deformation vibration of Si-O-Al bonds, Si-O and Si-Mg-Fe-O.

Examination of the thermal analysis curve of the purified sodium bentonite, shows, in the field of low temperatures, the existence of a 137°C intense endothermic phenomenon, this phenomenon is linked to the starting zeolite and the hygroscopic water of bentonites. Mass loss that accompanied these thermal accidents is very important; it is ~13.54% of the initial mass. Another endothermic phenomenon of low intensity occurs at a temperature of 640°C. It corresponds to the departure of the structural water. The mass loss associated with this phenomenon is ~3.62% of weight. The differential thermal analysis (DTA) curve also exhibits an exothermic accident to 894.25°C due to the crystallization of the bentonite.

The DTA curve relating to the Brute bentonite presents two endothermic phenomena at 100 and 240°C. This duplication is due to the presence of two types of water molecules, these are respectively hygroscopic and zeolitic water. Two other endothermic phenomena of low intensity occur in the area of average temperature 580 and 680°C correspond respectively to the strongly retained water and water of constitution. The DTA curve also shows a broad exothermic accident in the temperature range of 820 and 930°C.

Adsorption isotherms

Adsorption isotherms of *L. angustifolia* components are shown in Figure 4, Adsorption decreased in the order:

2-beta pinene > alpha thujon > camphor > L- linalool > fenchol > (Z E) alpha farnesene > alpha pinene > Cis linalool oxide > Trans alpha bergamotene > camphene > pirille alcohol > 1-Cis calamenene > beta eudesmol > Trans beta farnesene > 4-7 dimethyl 1 tetra lone.

The other compounds are: sabinene, (+) carvone, 1methyl adamantine, cryptone, 1-alpha terpineol, alpha campholene aldehyde, 1-4 terpineol, verbinone, cuminic aldehyde, (-) alpha campholenic acide, beta selinene, 1-4 norcadin-5-ene-4-one isomer B show a total adsorption of sodium on bentonite.

The adsorption isotherms also show the existence of an over saturation for 2-beta pinene and 1-8 Cineol which have the highest concentrations. The same phenomenon is observed for pirille alchool, 4-7 dimethyl tetra-lone and Beta eudesmol, over saturation of the last three is due to the saturation of all active sites by other most concentrated components as the 2-bêta pinene, 1-8 Cineol... The rest of the components as: verbenene, Limonene, Mcymene, beta bisabolene, calarene and Cis alpha bisabolene, have no affinity for the bentonite; thus, their adsorption is very low.

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 (Figure 4).

Langmuir and 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 (Puls, et al., 1991) 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 (Allen and Mckay, 1987).

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, 1888) and (Freundlich, 1909) 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 (Ho and Mackay, 1998).

The Langmuir equation model assumes that the solid adsorbent has a limited adsorption capacity (q_m) , all the active sites are identical, they are only a complex of solute-molecule (monolayer adsorption) and that there is no interaction between the adsorbed molecules.

Freundlich:

$$q_e = K_F C_e^{1/n} \tag{6}$$

$$Log qe = Log KF + n Log Ce$$
(7)

Another use of the results by the Freundlich isotherm is to draw logarithmic scale variations in the distribution coefficient K_d according to q_e

$$Log \ Kd = \left(\frac{1}{n}\right) Log \ KF + \left[\frac{(n-1)}{n}\right] Log \ qe \tag{8}$$

The Langmuir model has two linear forms: Form I:

$$\frac{Ce}{qe} = \frac{1}{KL\,qm} + \left(\frac{1}{qm}\right)Ce\tag{9}$$

Form II:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qm*KL*Ce} \tag{10}$$

(a) Total adsorption



Figure 4. (a) Major components in *Lavandula angustifolia* essential oil with adsorption isotherms. (b) Major components in *Lavandula angustifolia* essential oil with total adsorption.

 C_{e} and qe are the equilibrium concentration and amount adsorbed, K_{L} is a direct measure for the intensity of the

adsorption process or related to the heat of adsorption $(dm^3 mg^{-1} \text{ or } L.mg^{-1})$, and q_m is a constant related to the





Beta Selinene

1-4-Norcadin-5-En-4-One Isomer B

Beta Bisabolene

Figure 4 Contd.

area occupied by a monolayer of absorbate, reflecting the limiting adsorption capacity (mg g⁻¹). A plot of C_e/q_e vs C_e, q_m and K_L can be determined from the slope and intercept. K_F is a constant for the system, related to the bonding energy.

 K_F can be defined as adsorption or distribution coefficient and represents the quantity of each compound adsorbed onto adsorbents for a unit equilibrium concen-

tration $(dm^3 mg^{-1})^{1/n}$ or $(mg g^{-1})$ In accordance with (Hasley, 1952), the relationship between K_F and q_m is:

$$K_{\rm F} = q_{\rm m} / C_0^{\rm n} \tag{11}$$

(qm) is the maximum adsorption capacity. The slope 1/n, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity (Haghseresht, 1998). A

	Model									
Compound		Freundlich		Langmuir						
	n	K _F	R²	ΚL	q m (theo)	q m (exp)	R²			
1 Cis Calamenene	0.255	17.939	0.7032	139.314	12.225	12.24	0.98562			
1-8 Cineol	4.051	1.445	0.83265	0.541	1207.318	1235.48	0.14605			
2 -β-pinene	0.513	2090.084	0.63727	3.262	2684.139	1506.143	0.5378			
4 7 Dimethyl	6.832	5.1 E ⁺¹¹	0.68509	148.214	11.206	7.154	0.11826			
α-Pinene	3.582	12.819	0.99216	4.032	130.548	147.9	0.62173			
α-Thujon	0.0744	1102.196	0.69709	313.374	1111.569	1107.82	0.99994			
β-eudesmol	1.672	2484.607	0.75252	25.548	23.579	8.5049	0.0528			
Camphene	2.838	3518.183	099214	7.279	39.479	31.56	0.05866			
Camphor	1.678	2.1651E ⁺⁵	0.93528	42.234	719.424	669.68	0.97415			
Cis Linalool Oxide	0.147	85.031	0.7147	175.412	68.966	67.88	0.99687			
Fenchol	1.093	4445.555	0.92506	18.930	298.507	185.039	0.43408			
Linalool	0.353	795.594	0.94472	333.749	272.480	362.03	0.95582			
Pirille alchool	3.047	1.593E ⁺⁶	0.75589	1405.113	25.867	18.21	0.79193			
Trans α-Bergamotene	0.449	157.524	0.99268	242.491	39.904	40.269	0.92397			
Trans β- farnesene	0.084	9.923	0.62409	1085.549	8.006	7.569	0.99547			
Z E α-farnesene	0.04	184.485	0.9988	176.1109	177.620	177.649	0.99989			

Table 3. Langmuir and Freundlich adsorption constants of Lavandula angustifolia oil on sodium modified bentonite.

 K_F , Adsorption or distribution coefficient; R^2 , Freundlich model and correlation coefficients; K_L , direct measure for the intensity of the adsorption process or related to the heat of adsorption; q_m (theo) and q_m (exp), limited adsorption capacity.

value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative for a cooperative adsorption (Fytianos et al., 2000).

A plot of Lnq_e vs. C_e enables the empirical constants K_F and 1/n to be determined from the intercept and slope of the linear regression. The two common isotherm models have been tested in the present study: Langmuir and Freundlich models. Applicability of the isotherm equations was compared in Table 3 by judging the correlation coefficients, R^2 :

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, 2-Beta pinene, 4-7 di-methyl-tetralone, Alpha Pinene, Beta eudesmol, camphene, Fenchol and Trans alpha Bergamotene. 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 *L. angustifolia* essential oil. The coefficients (R^2) for Langmuir model shows that the sorption of: 1-Cis Calamenene, alpha Thujon, camphor, Cis Linalool oxide, L-Linalool, Pirille alcohol, Trans beta farnesene and (Z E) alpha farnesene can conform to the Langmuir model.

Considering some individual components, they presented the highest adsorption capacity for 2-beta pinene with qm = 1506.143 ug/g et K_L = 3.262, K_F = 2090.084 and n = 0.513 puis 1-8 Cineol with qm =1235.48 ug/g, K_L = 0.541, K_F = 1.445 and n = 4.051. α -Thujon, with qm = 1107.82 ug/g, K_L = 313.374, K_F = 1102.196 and n = 0.0744.

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}= 12.225 ug/g and qm_{exp} = 12.24 ug/g), 1-8 Cineol (qm_{theo}= 1207.318 ug/g and qm_{exp} = 1235.48 ug/g), 4-7 dimethyl tetralone (qm_{theo}= 11.206 ug/g and qm_{exp} = 7.154 ug/g), α -Thujon (qm_{theo}= 1111.569 ug/g and qm_{exp}=1107.82 ug/g), Cis linalool oxide (qm_{theo}= 68.966 ug/g and qm_{exp} = 67.88 ug/g), Trans α -Bergamotene (qm_{theo}= 39.904 ug/g and qm_{exp} = 40.269 g/g), Trans β - farnesene (qm_{theo} = 8.006 ug/g and qm_{exp} = 7.569 ug/g) (Figures 5, 6, 7 and 8).

Conclusion

The terpenes: 2-beta pinene, alpha thujon, camphor, Llinalool, 1-8 cineol was absorbed by bentonite in higher amounts than others mono-terpenes. 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 depended on the particle size fractions; the finer fractions adsorbed higher amounts. 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 other monoterpene hydrocarbons. The adsorption isotherm of the terpenic compound on



Figure 5. Adsorption isotherms of Lavandula angustifolia components on sodium modified bentonite.



Figure 6. Adsorption isotherms of Lavandula angustifolia components on sodium modified bentonite (Zoom 1).



Figure 7. Adsorption isotherms of Lavandula angustifolia components on sodium modified bentonite (Zoom 2).



Figure 8. Adsorption isotherms of Lavandula angustifolia components on sodium bentonite (Zoom 3).

bentonite was fitted with the Langmuir like: 1 Cis calamenene, alpha thujon, camphor, Cis linalool oxide, linalool, pirille alcohol, trans beta farnesene, (Z E) alpha farnesene) and Freundlich model like: 1-8 Cineol, 2 Beta pinene, 4-7 dimethyltetralone, alpha pinene, beta eudesmol, camphene, Fenchol and Trans alpha bergamotene.

Conflict of Interests

The author(s) have not declared any conflict of interest.

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