PROPRIETĂȚILE A DOI ZEOLIȚI NATURALI MODIFICAȚI CU ULEI ESENȚIAL DE OREGANO
THE PROPERTIES OF TWO NATURAL ZEOLITES MODIFIED WITH OREGANO ESSENTIAL OIL

DURMUŞ ALPASLAN KAYA[1], ZINA VULUGA[2*], CRISTIAN ANDI NICOLAE[2], CONSTANTIN RADOVICI[2], MĂDĂLINA GEORGIANA ALBU[3*]

[1]*Mustafa Kemal University, Faculty of Agriculture, Department of Field Crops, 31034, Antakya-Hatay, Turkey*
[2]*Institutul Național de Cercetare Dezvoltare pentru Chimie şi Petrochimie - ICECHIM, Spl. Independenței 202, 060021, Bucureşti, România*
[3]*INCDTP - Sucursala Institutul de Cercetare Pielarie Incaltaminte,Departament Colagen, Str. Ion Minulescu 93, 031215, Bucureşti, România*

The aim of this study was to prepare zeolites modified with oregano essential oil and to establish their morphological and thermal properties as well as the release ability of essential oil from zeolites. The chemical composition of oregano oil was determined by GS-MS. The crystalline structure and chemical composition of two natural zeolites were performed by X-ray diffraction (XRD) and X-ray fluorescence (EDXRF). Both natural zeolites presented similar structure with clinoptilolite type. The thermal characteristics of oregano oil, zeolites and their combination were carried out by thermogravimetric analyses (TGA). The oregano oil was loaded in zeolite in order to improve its stability. It gradually evaporated so that the percentage of oil removed after 2h from zeolites was two times lower than itself evaporation. This property allows to the natural combination between zeolite and essential oil to be used as basic material in medical, pharmaceutical, cosmetic and food industry.

Scopul acestui studiu a fost obținerea unor zeoliți modificați cu ulei esențial de oregano şi determinarea proprietăților morfologice şi termice, precum şi capacitatea de eliberare a uleiului esențial din zeoliți. Compoziția chimică a uleiului de oregano a fost determinată prin GS-MS. Compoziția chimică şi structura cristalină a celor doi zeoliți naturali au fost determinate prin difracție de raze X (XRD) şi fluorescență de raze X (EDXRF). Ambii zeoliți naturali au prezentat o structură similară cu tipul de clinoptilolit. Caracteristicile termice ale uleiului de oregano, zeoliților şi combințiile lor au fost determinate prin analize termogravimetrice (TGA). Ulei de oregano a fost încorporat în zeolit, în scopul de a-i îmbunătăți stabilitatea. Acesta s-a evaporat treptat, astfel încât procentul de ulei eliberat după 2h din zeoliți a fost de două ori mai mic decât evaporarea în sine. Această proprietate permite combinațiilor naturale dintre ulei esențial şi zeolit să fie utilizate ca materiale de bază în industria medicală, farmaceutică, cosmetică şi alimentară.

Keywords: *zeolite, essential oil, thermal analyses*

1. Introduction

Natural zeolites have enjoyed considerable attention over the last decade, due to the good performance of this material in ion exchange, adsorptive and biocatalytic processes, together with its high chemical stability [1]. Zeolites are aluminosilicates with a uniform microporous and rigid three-dimensional crystalline structure (similar to a honeycomb) consisting of cage and channels framework [2]. Natural zeolites are the most important inorganic cation exchangers [3]. Clinoptilolite, the most abundant natural zeolite, has a high cation exchange capacity, high temperature resistance, selectivity and compatibility with the natural environment. Researchers have shown zeolites to be natural, non-toxic, viable carriers, controlled release agents and adjuvant for drugs, thus showing their potential for biomedical applications [4]. Medicine today is looking for natural treatment for all type of disease. So far bioceramics were tested to be used in biomedical applications [5, 6].

Essential oils are widely distributed in nature and are found in *Rutaceae* (citrus spp), *Asteraceae* (chamomile), *Myrtaceae* (eucalyptus), although the majority of plants with essential oils are found in the *Lamiaceae* (mint, lavender, thyme, rosemary) and *Apiaceae* (fennel) families [7,8].

Essential oils are aromatics or odorous, obtained from parts of plants, such as herbs, seeds, leaves, buds, woods, roots, flowers, twigs, bark, and fruits. Because the essential oils from aromatic and medicinal plants have potentially useful therapeutic properties (antibacterial, antiviral, antifungal, and antimicrobial), they are widely used in the pharmaceutical, food, and perfume industries [9].

They are also used in medicinal products for adding taste or smell or to suppress the less

*Autori corespondenți/*Corresponding authors,*
Tel.: + 40-21-3163068; +40-21-3137141, e-mail: zvuluga@yahoo.com; albu_mada@yahoo.com

desirable medicated flavour [10]. A total 38 oregano species are recognized all over the world. Most of the oregano species, over 75%, are found in the East Mediterranean subregion [11]. The flora of Turkey has 23 species of oregano (16 endemic) [12]. Due to the variability in chemical and aroma characteristics, Oregano plants belonging to different species and ecotypes (biotypes) are widely used in agriculture, pharmaceutical and cosmetic industries as a culinary herb, flavouring substances of food products, alcoholic beverages and perfumery for their spicy fragrance [13]. Oregano species are also used for production essential oil and the remaining water is taken orally to reduce blood cholesterol and glucose levels and for cancer treatment [14].

In folk medicine, it is also used as stimulant, analgesic, antitussive, expectorant, sedative, antiparasitic and antihelminthic [15]. The green leaves of the oregano are rich in essential oil, which confers its characteristic and fragrance. The extraction product can vary in quality, quantity and composition according to climate, soil composition, geographical location, seasonal variation, plant organ, age and vegetative cycle stage, harvesting time [16]. *Origanum syriacum* L. var. *bevanii* is one of the widely distributed varieties growing in the Southeast of Turkey [7]. It is an important herb rich in phenolic compounds with strong antioxidant and antibacterial properties [17]. However, there have been no attempts to study the chemical composition and biological activities of essential oils and extracts from O. *syriacum* L. var. *bevanii* plants collected from the Eastern Anatolia region of Turkey up to now. In the presence of oxygen from the air, essential oils undergo undesirable deterioration reactions. The products formed by oxidation reactions are strongly allergenic with less biological activity than the original compounds [18,19]. For sustaining the stability and efficacy of essential oils, their association with different protecting matrices has been widely studied [20, 21].

Some authors have studied the association of essential oils with chitosan, for sustained stability and prolonged release of essential oils from pharmaceutical formulations [22]. In this study, we used oregano oil adsorbed on zeolite. The zeolite provides a time delay to release of the oregano oil. Based on this property the natural combination between zeolite and oregano oil could be used as basic material for adding into plastic, paints, synthetic fabrics and may be bonded to surface such as stainless steel [23] and could be used in medical, pharmaceutical, cosmetic and food industry.

The aim of this study was to characterise different commercially zeolites and oregano essential oil and to prepare mixtures from them in order to establish their morphological and thermal properties as well as the release ability of essential oil from zeolites.

2. Experimental

2.1. Oregano oil extraction

Origanum syriacum L. var. *bevanii* were collected during the blooming period in the province of Hatay, the east Mediterranean part in the south of Turkey. They were dried at room temperature in dark place at the Laboratory of Medicinal and Aromatic Plants, Faculty of Agriculture, Mustafa Kemal University.

The oregano essential oils were produced by the Clevenger hydrodistillation method. The dried plant materials (100 g) were placed in a distillation apparatus with distilled water and hydrodistilled for 2 h. About 3% of oregano essential oil was obtained and stored at 4^0C until used for GC analyses.

2.2. Zeolites

Two samples of natural zeolites from different commercially companies were used in this study. They were named as Z-1 and Z-2 and were used as received in the experiments or after drying under vacuum. The sample Z-1, a tribomechanically activated zeolite clinoptilolite, was supplied by TRIBOMIN d.o.o. Osijek, Croatia. The samples Z-2 was supplied by ORTAR Organik Tarim Turkey.

2.3. Determination of chemical composition of oregano oil by GC-MS

Analysis of the essential oil carried out by using Thermo Scientific ISQ Single Quadrupole Gas Choromatograph equipped with MS, auto sampler and TR-5MS (5% Phenyl Polysilphenylene-siloxane, 0.25 mm x 30 m i.d, film thickness 0.25).The carrier gas was helium (99.9%) at a flow rate of 1 mL/min; ionization energy was 70 eV. Mass range m/z 1.2-1100 amu. Data acquisition was scan mode. MS transfer line temperature was 250^{o}C, MS Ionization source temperature was 220^{o}C, the injection port temperature was 220^{o}C. The samples were injected with 250 split ratio. The injection volume was 1μl. Oven temperature was programmed to from 50^{o}C to 220^{o}C at 3^{o}C /min. The structure of each compound was identified by comparison of their mass spectrum (Wiley) data was handled through using of Xcalibur software program. The retention indices (RIs) were calculated for all volatile constituents using a homologous series of *n*-alkane standard solutions C_8-C_{20} (Fluka, product no. 04070) and C_{21}-C_{40} (Fluka, product no. 04071).

2.4. X-ray diffraction (XRD)

Identification of mineral components in the zeolite samples was performed using X-ray diffraction analysis (XRD) on the powder samples. The XRD patterns were recorded on a DRON UM1 diffractometer using an iron filter for the CoK_α radiation (1.79021 Å).

2.5. X-ray fluorescence (EDXRF)

Chemical composition of the natural zeolites was determined by X-ray fluorescence analysis. EDXRF was performed with an energy dispersive X-ray fluorescence spectrometer, EDXRF PW4025, Minipal 2-PANalytical, with a Si(PIN)-detector, having a resolution of 150 eV at 5.89 keV (Mn-K_α-line).

2.6. Thermogravimetric analyses (TGA)

The thermal characterization of the samples of essential oil, zeolites and their combination was carried out with a TA Q5000 IR Instrument (weight of the sample: 15 mg; heating rate: 10^0C / min in air atmosphere).

2.7. Oregano oil modified zeolite preparation

The zeolites and oregano essential oil in 1:0.3 ratios were mixed using zeolites both as such and after drying under vacuum. Vacuum drying was carried out in order to remove water molecules from the channels of zeolite and to allow to the oil to penetrate easily and take the place of water. The mixtures of oregano oil with Z-1 and Z-2 were powdery.

3. Results and discussion

3.1. Qualitative determination of oregano essential oil components

According to GC-MS results, 25 different components were identified in the oregano essential oil. The main components (Table 1) are phenolic compounds: thymol (27.66%) and carvacrol (24.71%) and the other determined characteristic ones are γ-terpinene (20.01%), cymol (13.24%), α-terpinene (4.12%), α-myrcene (2.37%), trans-caryophyllene (1.21%), α-pinene (1.04%).

Table 1

Composition of Origanum syriacum L. var. bevanii essential oil / *Compoziția uleiului esențial de Origanum syriacum L. var. bevanii*

RT	RI	Component	% peak area *% aria picului*
3.64	1027	α-pinene	1.04
3.70	1032	thujene	0.96
4.35	1073	camphene	0.14
5.15	1112	β-pinene	0.15
6.09	1150	sabinene	0.09
6.50	1168	α-myrcene	2.37
6.90	1184	α-terpinene	4.12
7.42	1200	α-terpinenyl acetate	0.43
7.69	1212	α-phellandrene	0.29
8.85	1249	γ-terpinene	20.01
9.09	1259	trans-ocimene	0.08
9.68	1276	cymol	13.24
10.04	1284	p-mentha-1,4(8)-diene	0.18
13.99	1395	3-octanol	0.58
16.15	1454	amyl vinyl carbinol	0.68
16.58	1467	trans-sabinene hydrate	0.28
19.73	1546	terpineol	0.11
19.90	1552	linalool	0.1
21.38	1588	trans-caryophyllene	1.21
21.78	1599	4-terpineol	0.92
24.07	1663	α-humulene	0.13
25.36	1711	isoborneol	0.37
34.87	1963	(-)-caryophyllene oxide	0.15
41.80	2252	thymol	27.66
42.60	2252	carvacrol	24.71

RT: Time retention/Timp de retinere

3.2. Zeolites characterization

X-ray diffractogram showed significant presence of clinoptilolite in the zeolite sample Z-1 (Fig. 1). X-ray diffractogram of natural zeolite Z-1 has been compared with the diffraction pattern for clinoptilolite (reference pattern: 39–1383, 25–1349, 47–1870). Fewer peaks in addition to those of clinoptilolite indicate high mineralogical purity (compared with Powder Diffraction File number, PDF# 25–1349 for clinoptilolite) of the sample and thus a higher percentage of clinoptilolite (~80%) [24].

Figure 2 shows that X-ray diffractograms for samples Z-1 and Z-2 are similar. Therefore, can be concluded that sample Z-2 is also a clinoptilolite but with a higher percentage of impurities (e.g. quartz with d = 4.2529 Å, at 2θ = 24.3° and d = 3.3442 Å, at 2θ = 31.05°, ASTM 33-1161).

The results of X-ray fluorescence analysis are presented in Figure 3. From fluorescence spectrum the sample Z-1 has the following chemical composition, in mass %: Na_2O, 2.1; K_2O, 4.1; Al_2O_3, 12.1; SiO_2, 67.1; loss of ignition, 6.5; MgO, 1.1; CaO, 4.9 and FeO, 2.7. The results have shown that the exchangeable ions of sample Z-1 are sodium, potassium, calcium and magnesium, as confirmed by Muzenda et al. [25].

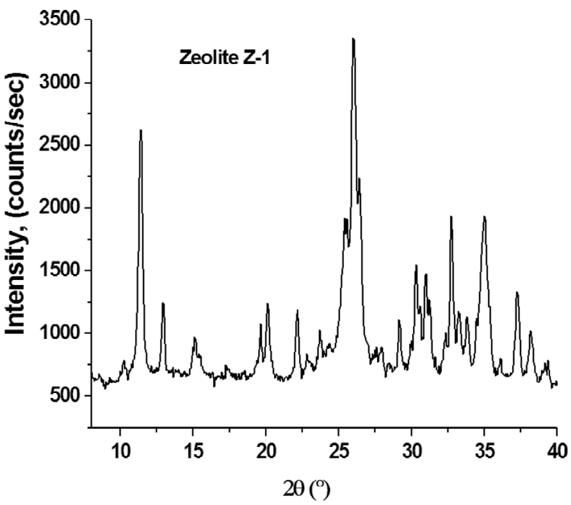

Fig. 1 - The X-ray diffractogram of zeolite Z-1 / *Difractograma de raze-X a zeolitului Z-1*

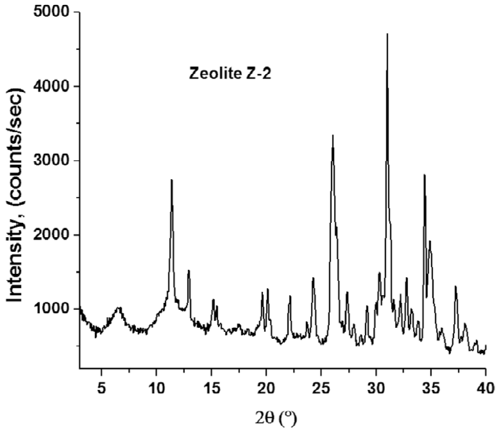

Fig. 2 - X-ray diffractogram of zeolite Z-2 / *Difractograma de raze X a zeolitului Z-2.*

3.3. Thermal characterization

In the range of the used temperature (20°C÷800°C), the zeolite samples exhibit four endothermic effects (Table 2). The first step of decomposition is in the temperature range of 20°C÷100°C and represents the loss of water from the surface of zeolite. The decomposition took place with maximum speed at 37°C for Z-1 and at 47°C for Z-2. The other steps of decomposition, from 100°C to 800°C represent the desorption of water from the clinoptilolite component of the sample. Gregory et al. [27] proved that there are three types of water associated with clinoptilolite: "external" water, "loosely bound zeolite" water, and "tightly bound zeolite" water. Corresponding to Breger et al. and Alietti et al. [28-30], the middle portion of TGA curve, between 50°C÷200°C represents desorption of "loosely bound zeolite" water and the high temperature portion, from 200°C÷700°C, represents the loss of "tightly bound zeolite" water.

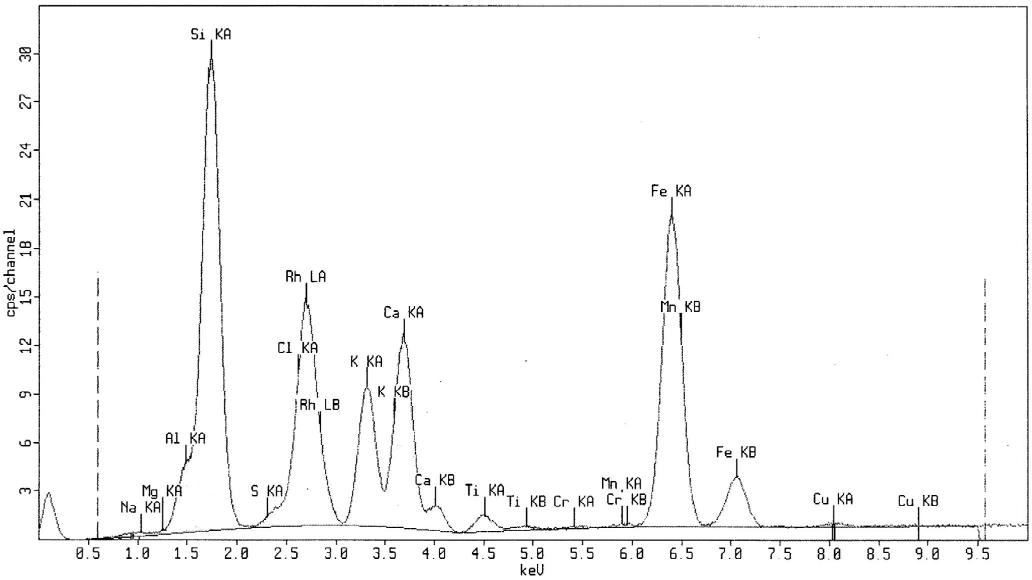

Fig. 3 - X-ray fluorescence spectrum for zeolite Z-1 / Spectru de fluorescență de raze X pentru zeolitul Z-1

Table 2

TGA results for Z-1 and Z-2 zeolite samples / *Rezultatele TGA pentru probele de zeolit Z-1 şi Z-2*

Sample/ Proba	T_{vdm} (°C)	The loss of mass on each step of decomposition (%) *Pierderea de masă pe fiecare treaptă de descompunere (%)*				R_{800} %
		I	II	III	IV	
		30÷100 °C	100÷260 °C	260÷520 °C	520÷800 °C	
Z-1	37	5,6	2,9	1,9	0,6	89,0
Z-2	47	4,6	3,2	2,1	1,5	88,6

T_{vdm}: Temperature at maximum rate of decomposition/ *Temperatura la viteza maximă de descompunere*;
R_{800}: Inorganic residue at 800°C/ *Reziduu anorganic la 800°C*

According to Gottardi [26] a zeolite having a Si/Al ratio greater than 4 is a clinoptilolite in which (Na+K) atoms per unit cell are predominant over Ca. For sample Z-1, the Si/Al ratio is 5.55 (mol/mol) and the corresponding ratio of (Na + K)/Ca is 1.27.

The samples Z-1 and Z-2 present similar thermal stability and in accordance with references. The amounts of total "zeolite" water (11% for Z-1 and 11.4% for Z-2) do not depend on the composition of sample. The presence of higher quantity of quartz in Z-2, it seems that does not

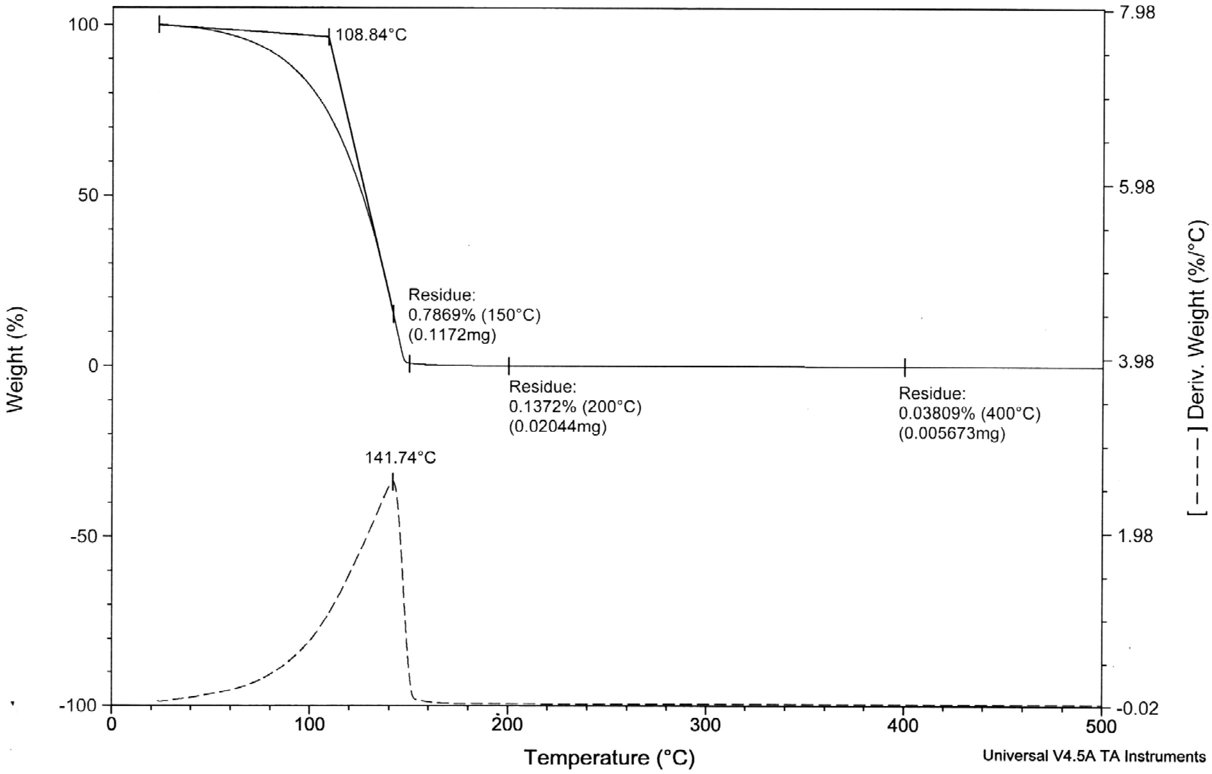

Fig. 4 - TGA results of oregano essential oil / Rezultatele TGA ale uleiului esențial de oregano

Table 3

The weight loss of oregano oil, zeolites and their combination
Pierderea de masă pentru uleiul de oregano, zeoliți și combinația acestora

Samples / *Probe*	Weight Loss / *Pierdere de masă* (%)				
	Room Temperature- *Temp. camerei-* 160°C	160-300°C	300-500°C	500-700°C	Residue (700°C)
oregano oil	99.6	0.2934	0.0885	0.0002	0
zeolite Z-1	6.856	2.171	1.393	0.6368	88.91
zeolite Z-1 - oregano oil	16.12	2.081	1.88	0.7823	79.07
zeolite Z-2	6.075	2.286	1.413	1.506	88.71
zeolite Z-2 - oregano oil	8.067	2.651	2.289	1.877	85.07

influence the total "zeolite" water. The TGA results are in accordance with X-ray diffraction.

The thermal stability of oregano oil (Fig. 4) shows that it starts to lose weight at room temperature and at 100°C lose about 80% from weight. Based on its behaviour we mixed the oil with zeolite in order to prevent fast decomposition of oil and to be released in time.

The amount of oil adsorbed on the zeolite surface or into cavities is revealed by thermogravimetric analysis in dynamic conditions. Table 3 shows that the oil is adsorbed more or less, depending on the composition of zeolite used.

The amount of adsorbed oil is higher for Z-1 than for Z-2. This behaviour can be explained by the presence of quartz, a neutrally charged inert mineral, without adsorption abilities, which is in higher quantity in Z-2. The oil adsorption on the zeolite samples after their prior drying in vacuum is practically the same. In mixtures the temperature at maximum rate of decomposition on the first step of decomposition (in the range of temperature 20÷100°C) has higher values (96°C for the mixture Z-1-oregano oil and 80°C for the mixture Z-2-oregano oil, compared with 37°C for Z-1 and 47°C for Z-2 zeolite samples).

3.4. The release properties of oregano oil

The release of oregano oil from the zeolites studied is evidenced by thermo gravimetric analysis, maintaining the samples in isothermal conditions, at 30°C for 2h. Then the temperature was increased at 710°C and samples were maintained at this temperature for 10 minutes to determine the exact amount of oil adsorbed by zeolite.

In comparison with oil, which evaporates

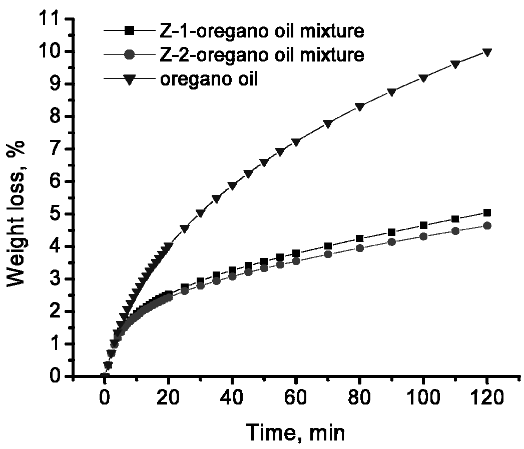

Fig. 5 - The release in time of the oregano oil from mixtures with zeolites, during 120 min at 30°C / *Eliberarea în timp a uleiului de oregano din amestecurile cu zeoliți, timp de 120 minute la 30^{0}C.*

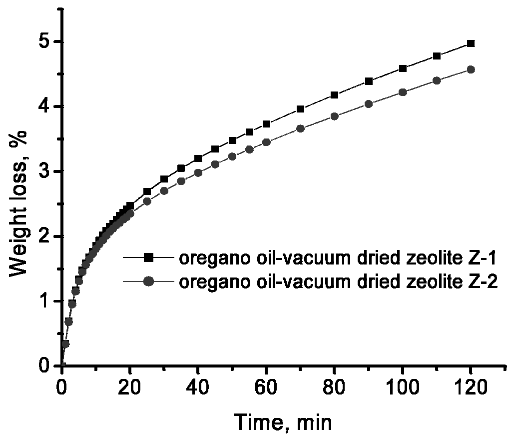

Fig. 6 - The release in time of the oregano oil from mixtures with vacuum dried zeolites, during 120 min at 30°C / *Eliberarea în timp a uleiului de oregano din amestecurile cu zeoliți uscați în vid, timp de 120 minute la 30^{0}C.*

very fast itself, the oil from the mixture with zeolite is more stable (Fig. 5 and 6). It gradually evaporates in such away that the percentage of oil released after 2h from zeolites is two times lower (about 5% from the mixtures, compared with 10% of the oil itself).

The percentage of oil released from both non-dried and dried in vacuum zeolites is not significantly different but it seems that the prior drying of zeolite favors the adsorption of oil (Fig. 7).

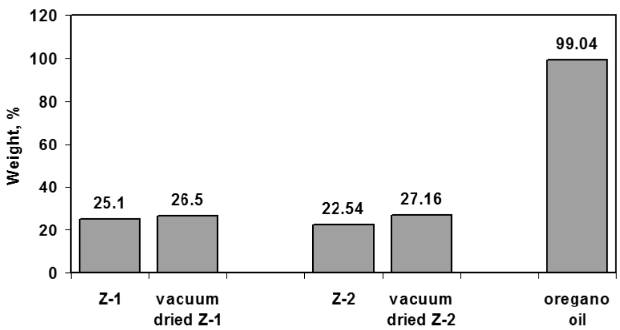

Fig. 7 - The total amount of oil released from zeolites-oregano-oil mixtures, after 10 min at 710°C / *Cantitatea totală a uleiului cedat din amestecurile zeoliți - ulei esențial de oregano, dupa 10 minute la 710^{0}C*

4. Conclusions

From the present work, it was found that the chemical composition of oregano essential oil extracted from *Origanum syriacum* L. var. *bevanii* was 27.66% thymol, 24.71% carvacrol, 20.01% γ-terpinene and 13.24% cymol. The natural zeolites studied have presented similar structure with clinoptilolite type. The results obtained have proven the efficiency of clinoptilolite in adsorption and releasing the oil. The oil itself evaporated fast and was less stable in comparison with the oil from the mixture with zeolite. It gradually evaporated so that the percentage of oil released after 2h from zeolites was two times lower than itself evaporation. This property allows to the natural combination between zeolite and essential oil to be used as basic material in medical, pharmaceutical, cosmetic and food industry.

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