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STUDY ON ENCAPSULATION OF LAVENDER OIL ESSENCE IN ZEOLITE AND BENTONITE MATRICES

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ABSTRACT

In the present study, four matrices for encapsulation of essential oils were investigated: based on natural zeolite, based on alkali-activated bentonite, based on combination of 60 mass % alkali-activated bentonite and 40 mass % natural zeolite and based on 60 mass % alkali-activated bentonite and 40 mass % limestone. All natural raw materials are from deposits in the Eastern Rhodopes, Bulgaria. These matrices were loaded with lavender oil essence in amounts of 5 mass %, 15 mass % and 30 mass % respectively. The change in weight was monitored after the matrices loaded with lavender oil essence and had been exposed to air for a certain period of time at room temperature (for 1, 2, 7, 9, 14 and 60 days). Using XRD and FT-IR, the preservation of lavender oil essence in the matrices was established after 1, 2, 7, 9, 14 and 60 days of exposure to air at room temperature. It can be concluded that after the granulation into spherical particles with a size of 1 to 2.5 mm, alkaline-activated bentonite can be successfully used as a matrix alone or with the addition of other natural mineral raw materials such as zeolite and limestone for encapsulation of essential oils.

Keywords: matrices, zeolite, bentonite, limestone, lavender oil essence, encapsulation.

INTRODUCTION

Essential oils are widely used in the medicine, the veterinary medicine, the food industry, the perfume and cosmetic industry, the chemical industry, etc. Aromatic substances are individual organic compounds or a mixture of them that have their own, most often pleasant odor and can transmit it to other substances when they come into contact with them. Natural oils are an aromatic mixture of volatile substances of essential oil plants, immiscible with water or partially soluble in it and easily soluble in organic solvents. The retention of the aroma of essential oils for a longer period is crucial for their application. Essential oils from aromatic and medicinal plants are widely distributed in nature and have potentially useful therapeutic properties - antibacterial, antiviral, antifungal and antimicrobial. Essential oils are mainly used in aromatherapy, healthcare, food and agriculture industry. Their antioxidant and antimicrobial properties make them attractive ingredients in various food and cosmetic products as flavours or preservatives against oxidation. Due to their anti-inflammatory, anti-allergic, antifungal properties the essential oils have therapeutic potential in cancer therapy, anxiety treatment or skin irritation problems [1 - 3].

In addition to their characteristic strong aroma, essential oils are sensitive compounds that can easily degrade when exposed to light, oxygen, and temperatures above 25^{o}C. The presence of oxygen from the air can affect their physical and chemical stability or cause a degradation process. The products formed by oxidation reactions are highly allergenic and have less biological activity than the original compounds. Low water solubility is one of the major limitations in the use of essential oils, therefore the concentration of these hydrophobic agents is low in the aqueous phase [1 - 3].

Encapsulation of aromas in porous materials is an innovative technology for preserving the aroma of essential oils, as well as for improving their thermal and oxidative stability. Currently, there is great interest in finding and researching new inexpensive and environmentally friendly matrices for encapsulation of essential oils for applications in healthcare, food, agriculture, etc. There is a lot of research on the application of various encapsulation matrices such as liposomes, chitosan, polymer nanoparticles, metal nanoparticles, carbon nanotubes, etc. [3].

Various aluminosilicate natural raw materials such as zeolite, bentonite, halloysite, quartz and their composites can be used as encapsulating materials for essential oils due to their abundance in nature, low cost, environmental friendliness, inertness and special porous structure [4 - 17]. Various aluminosilicate natural raw materials such as zeolite, bentonite, halloysite, quartz and their composites can be used as encapsulating materials for essential oils due to their abundance in nature, low cost, environmental friendliness, inertness and special porous structure [4 - 17]. Zeolites possess distinctive ion exchange and adsorption capabilities, along with a robust crystalline framework composed of channels, cavities, and nanopores arranged in a precise pattern. They offer a high surface area and demonstrate excellent thermal and acid stability. Their low toxicity in biological environments makes them suitable for biomedical applications, including use as antimicrobial agents, drug delivery carriers, and in therapeutic treatments. Thanks to their molecular sieve-like structure and cost-effectiveness, zeolites are widely used in various areas such as membranes, detergents, adsorbents, and catalysts. The integration of essential oils into zeolitic frameworks represents a promising alternative to conventional antibiotics, offering antimicrobial efficacy without contributing to the development of microbial resistance [4 - 8]. Bentonites, which are natural hydroaluminosilicates, are also a cheap and environmentally friendly matrix material suitable for encapsulating essential oils. The main clay mineral in bentonite is montmorillonite. Crystalline clay minerals consist of layers - tetrahedral, made up of tetrahedra [SiO_4] and octahedral [AlO_6]. A characteristic feature of the structure of montmorillonite is the penetration between the layers of water molecules and other polar molecules (from some organic substances), which cause expansion (swelling of the lattice) along the “c” axis. The most characteristic properties of bentonites, in addition to high plasticity, are high adsorption capacity and swelling capacity, and high ion-exchange capacity. The most common impurities in them are quartz, calcite, plagioclase, etc. [9 - 14]. Encapsulation is considered an effective method for preserving the quality of sensitive substances and improving essential oil delivery systems, allowing for controlled release of the ingredients. Encapsulation helps reduce evaporation or slows down the mass transfer of volatile compounds to the external environment by modifying the physical characteristics of the material inside the core of the particles. This innovative technology providing controlled and targeted release of active ingredients and improving shelf life of essential oils [15 - 17].

The purpose of this article is to study the encapsulation of lavender oil essence in natural inorganic matrices based on zeolite and bentonite.

EXPERIMENTAL

Materials

In the present study, four matrices based on natural inorganic raw materials were prepared, which were designated by the following numbers: 1 - matrix based on natural zeolite; 2 - matrix based on alkali activated bentonite with 2 mass % Na_2CO_3; 3 - matrix based on 60 mass % alkali activated bentonite and 40 mass % natural zeolite; 3 - matrix based on 60 mass % alkali activated bentonite and 40 mass % limestone. All natural raw materials come from deposits in the Eastern Rhodopes, Bulgaria. Matrix 1 was fractionated by crushing and sieving natural zeolite to obtain a fraction with a zeolite particle size of 1 to 2.5 mm. Matrices 2, 3 and 4 were granulated with a toothed agitator type granulator to obtain spherical granules with a particle size of 1 to 2.5 mm. Fig. 1 shows the granulator used for the matrices' granulation. The initial matrices for encapsulation are shown in Fig. 2. The lavender oil essence (Lavender III Lorb 2038295) for encapsulation in matrices is used in this study. It contains Linalool (EC 201-134-4), Linalyl acetate (EC 204-116-4), Coumarin (EC 202-086-7), Eucalyptol (EC 207-431-5). The density of lavender oil essence is 1.1 g cm^{-3}.

Experimental methodology

5, 15 and 30 mass % of lavender oil essence to 120 g of each matrix (from 1 to 4) were added separately with a pipette in plastic boxes /containers/, which were kept closed for 24 h, shaking from time to time. Then, samples in closed containers for analysis with XRD and FT-IR were taken. From the matrices thus loaded with lavender oil essence, 20 g samples were weighed on an analytical balance and placed in different boxes with lids. They were kept open for 1, 2, 7, 9 and 14 days respectively and then closed and weighed. The change in weight was calculated after the matrices with the lavender oil essence had been exposed to air for a certain period. The weight change was calculated using the following formula:

$$W_c = \frac{m_0 - m_1}{m_0}\,100, \%$$

where: W_c is the change in weight, %; m_o - the weight of the matrix in g 24 h after being loaded with lavender oil essence in amounts of 5, 15 and 30 mass %; m_1 - the weight of the matrix in g loaded with lavender oil essence in amounts of 5, 15 and 30 mass % after exposure to air for 1, 2, 7, 9 and 14 days.

Analysis methods

The initial materials and encapsulated matrices with lavender oil essence in amounts of 5, 15 and 30 mass % after exposure to air for 1, 2, 5, 7, 9, 14 and 60 days were analysed with XRD and FT-IR. Powder X-ray diffraction analyses were performed with PAN analytical EMPYREAN diffractometer system with a goniometer radius of 240 mm, operating at 40 kV and 30 mA, theta-theta geometry, with Cu Kα radiation (λ = 1.5406), equipped with 3D-pixel detector. The Fourier-transform infrared (FT-IR) spectra were recorded in the 4,000 - 400 cm^{-1} range by using a FT-IR spectrometer Varian 600-IR.

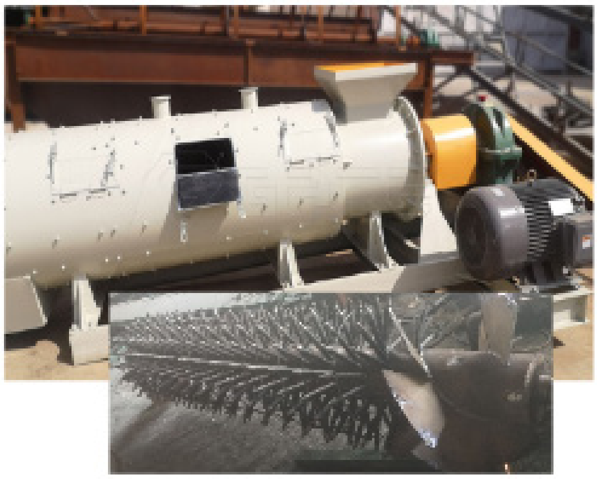

Fig. 1. Toothed agitator type granulator, with which granulated matrices 2, 3 and 4 were obtained.

Fig. 2. Initial matrices used for encapsulation of essential oils.

RESULTS AND DISCUSSION

Fig. 3a, b and c show the results of X-ray diffraction of the initial raw materials as natural zeolite, alkali-activated with 2 mass % Na_2CO_3 bentonite and limestone. The natural zeolite used for encapsulation of lavender oil essence contains mainly the mineral clinoptilolite and a small amount of opal. The main mineral in bentonite is montmorillonite. As secondary minerals are also present calcite, clinoptilolite, quartz and plagioclase in small amounts. The limestone contains only calcite. Fig. 4 shows the ATR-FTIR of lavender oil essence. The figure shows the characteristic absorption bands of lavender essential oil. In the spectral region of 2800 - 3100 cm^{-1}, absorption bands at 2875 cm^{-1}, 2937 cm^{-1}, and 2968 cm^{-1} were observed, which correspond to $-CH_2$ stretching, whereas the band at 3450 cm^{-1} refers to O-H stretching vibrations. The most intense absorption band in the spectrum appeared at 1740 cm^{-1} and it was related to C=O stretching vibrations. The FT-IR band at 1640 cm^2 belongs to C=C stretching vibration. In the region 400 - 1500 cm^{-1}, FT-IR bands were observed at 687 cm^{-1}, 835 cm^{-1}, 917 cm^{-1} associated with (C-H vibrations), 990 cm^{-1} ($-CH_2$ vibrations), 1112 cm^{-1}, 1168 cm^{-1}, 1235 cm^{-1} (C-O stretching vibrations), 1375 cm^{-1}, 1420 cm^{-1}, 1450 cm^{-1} (C-H bending vibrations). The bands between 1500 cm^{-1} and 1000 cm^{-1} are associated with C-O-H bending and C-H bending of the aliphatic groups (CH_2).

The following Fig. 5 - 8 show the change in weight of the matrices with different content of lavender oil essence for a certain period of exposure to air from 1 to 14 days.

The figures show that with increasing the exposure of the matrices loaded with the oil essence to air, a decrease in the weight of the sample is observed due to the evaporation of the solvent in the lavender essence

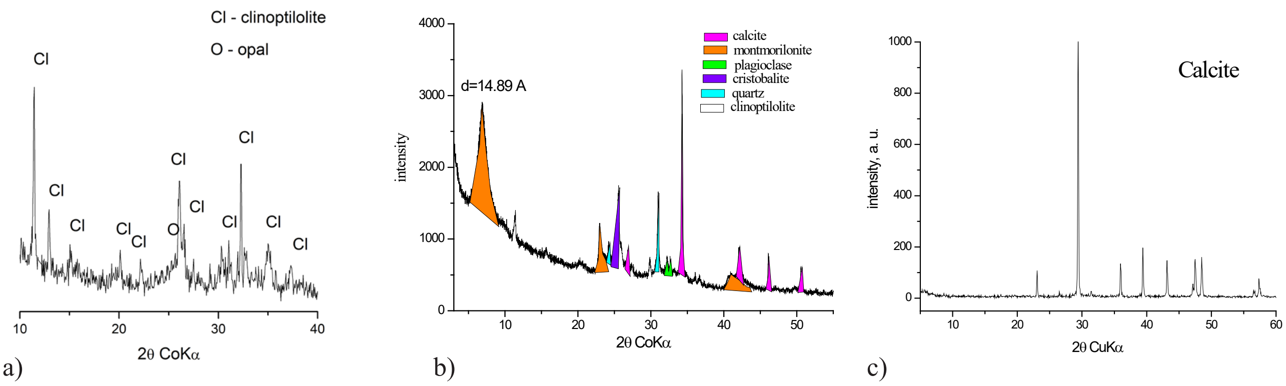

Fig. 3. XRD of zeolite (a) alkaline activated bentonite, (b) and limestone (c) from deposits in Eastern Rhodopes, Bulgaria.

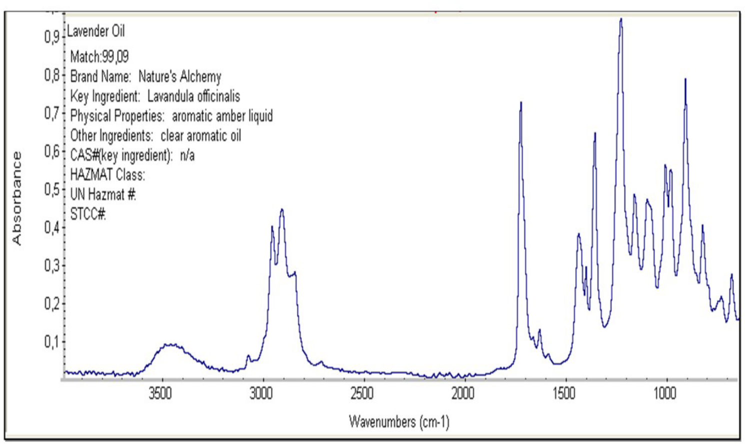

Fig. 4. ATR-FT-IR of lavender oil essence.

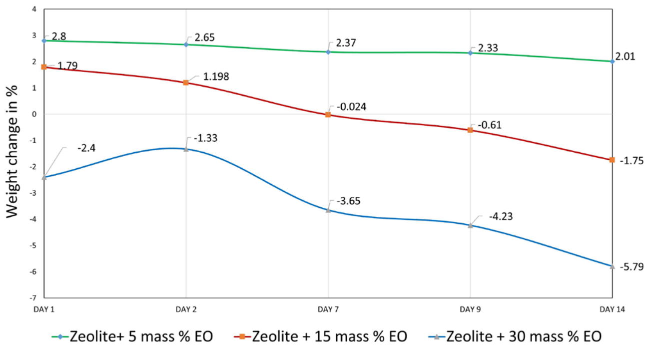

Fig. 5. Change in the weight of matrix 1 (zeolite) charged with lavender oil essence in amounts of 5, 15 and 30 mass % after a stay at air at room temperature for 1, 2, 7, 9 and 14 days.

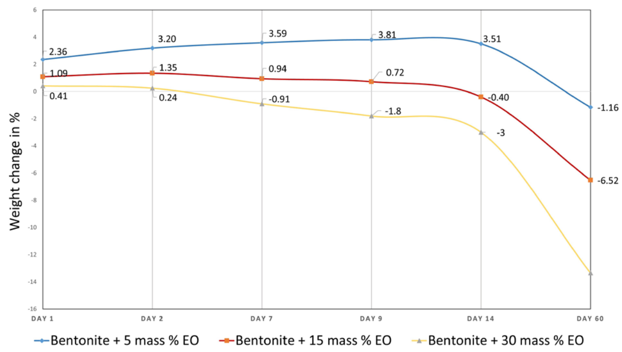

Fig. 6. Change in weight of matrix 2 (bentonite) with lavender oil essence in amounts of 5, 15 and 30 mass % after a stay at air at room temperature for 1, 2, 7, 9 and 14 days.

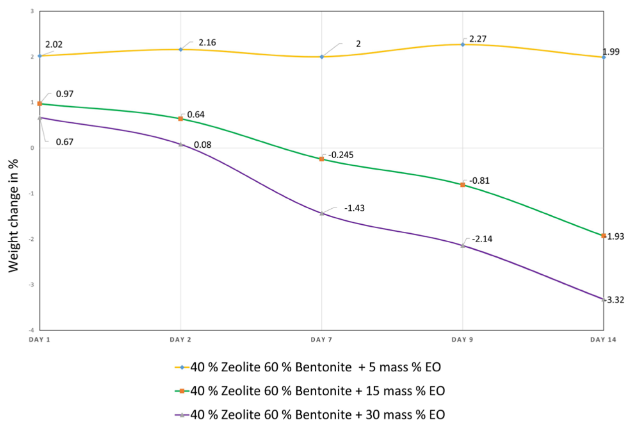

Fig. 7. Change in weight of matrix 3 (60 mass % bentonite and 40 mass % zeolite) with lavender oil essence in amounts of 5, 15 and 30 mass % after a stay at air at room temperature for 1, 2, 7, 9 and 14 days.

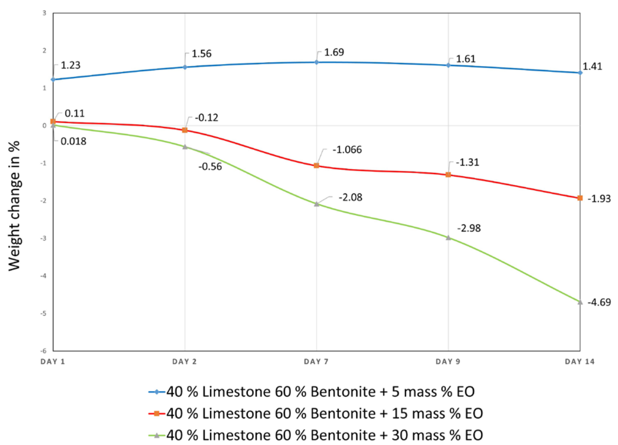

Fig. 8. Change in weight of matrix 4 (60 mass % bentonite and 40 mass % limestone) with lavender oil essence in amounts of 5, 15 and 30 mass % after a stay at air at room temperature for 1, 2, 7, 9 and 14 days.

and the moisture of the sample. The greater the amount of oil essence, the more clearly the trend is expressed. In the samples with 5 mass % essence, sorption of moisture from the atmosphere and a slightly increased weight of the samples are observed in the initial period of exposure.

FT-IR confirms the retention of lavender essential oil in the matrices. Fig. 9a shows the FT-IR spectra of matrix 1 (natural zeolite), and Fig. 9b shows the FT-IR spectra of matrix 2 (alkali activated bentonite) with 15 mass % lavender oil essence after exposure to air for 1, 2, 7, 9, 14 and 60 days. The figures show that the bands in the region 2875 - 2976 cm^{-1} characteristic of lavender oil and corresponding to $-CH_2$ stretching in bentonite are preserved even after 60 days of exposure to air, while in zeolite they decrease and are very weak after 60 days of exposure to air.

Fig. 10 shows the diffractograms of granular alkali activated bentonite (Matrix 2) loaded with 5, 15 and 30 mass % lavender oil essence. The first peak of montmorillonite (hkl - 001) in the initial bentonite has an interplanar distance of d = 14.89 Å. When loading bentonite with 5, 15 and 30 mass % lavender oil essence, a peak shift was observed, respectively to d = 15.00 Å (5 mass % lavender oil essence), d = 15.62 Å (15 mass % lavender oil essence) and d = 15.94 Å. (30 mass % lavender oil essence). This peak shift shows that the lavender oil essence enters between the layers of bentonite in its structure and is retained in the structure of bentonite, thus preserving its aroma for a

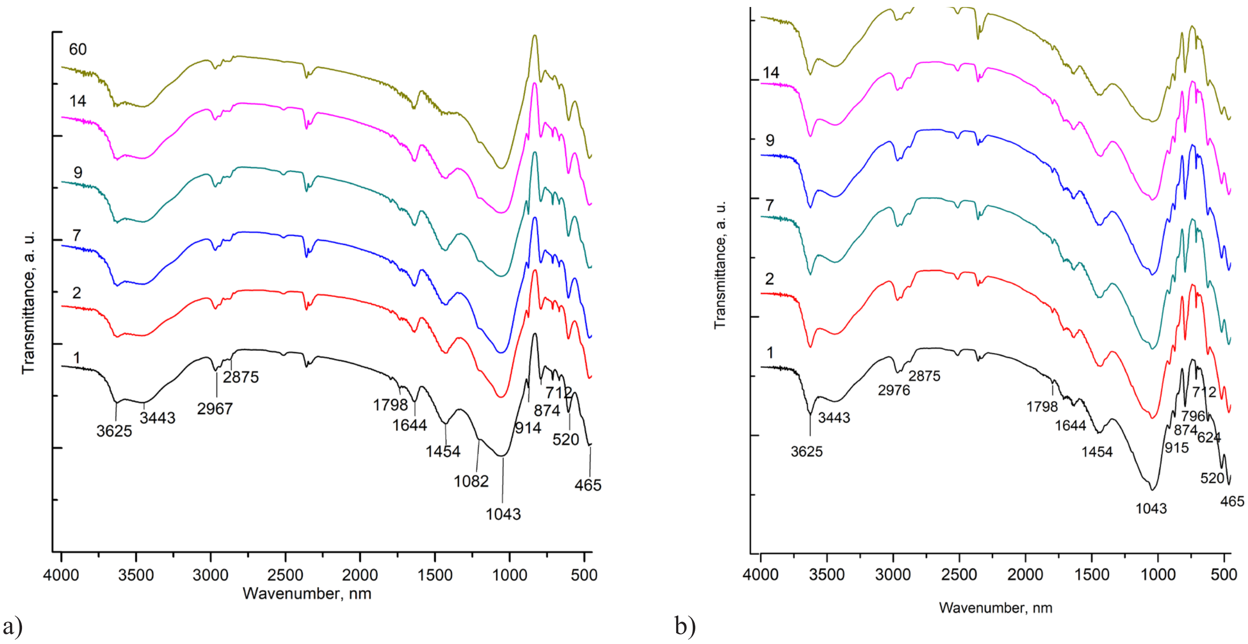

Fig. 9. FT-IR of matrix 1 (natural zeolite) (a) and matrix 2 (alkali activated bentonite) (b) with 15 mass % lavender oil essence after exposure to air for 1, 2, 7, 9, 14 and 60 days.

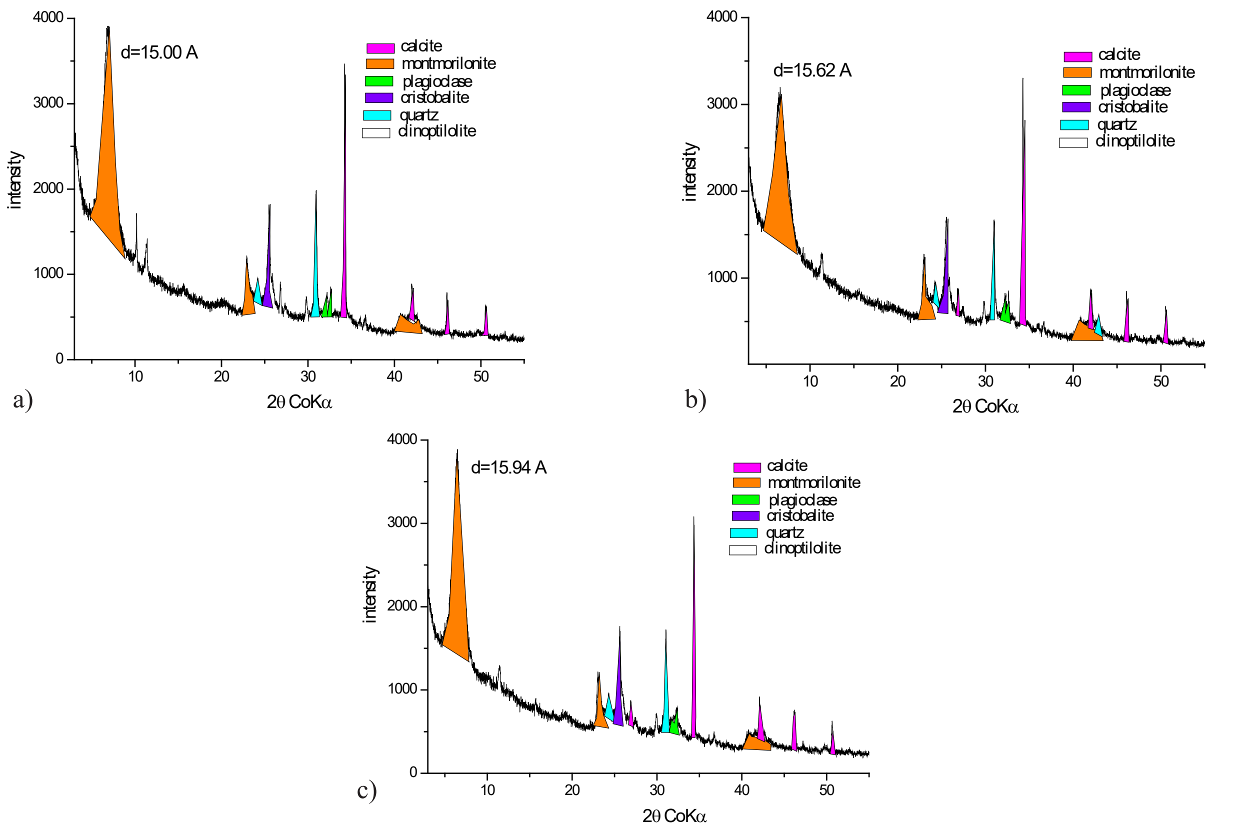

Fig. 10. Diffractograms of granular alkali activated bentonite (matrix 2) loaded with 5 (a), 15 (b) and 30 (c) mass % lavender oil essence.

longer period of time without being able to evaporate. In fact, organic activation of bentonite occurs and the alkali-modified bentonite turns into organo bentonite. The matrices based on bentonite with zeolite (matrix 3) and limestone (matrix 4) have a behaviour like a matrix composed of bentonite only.

CONCLUSIONS

The present study proved that matrices based on natural zeolite and alkali-activated bentonite can be used to encapsulate essential oils for their slower release and longer aroma retention. In the present study, four natural inorganic matrices for the encapsulation of essential oil essences were investigated. By the methods of XRD and FT-IR it has been proven that the better matrix for encapsulation of essential oils is alkali-activated bentonite. FT-IR established the retention of lavender essential oil in the matrice from alkali activated bentonite with 15 mass % oil essence after 60 days of exposure to air. By XRD have been established that the organic molecules of the lavender oil essence were inserted between the layers of the montmorillonite. This is due to that the alkaline-modified bentonite becoming organo bentonite. An important condition for obtaining a good matrix for encapsulating essential oils is also and the granulation of the material from which the matrix is made.

In conclusion, it can be noted that alkaline-activated bentonite after granulation to a spherical particle size of 1 to 2.5 mm can be successfully used as a matrix alone or with the addition of other natural mineral raw materials such as zeolite and limestone for encapsulation of essential oils, since the main mineral in bentonite, montmorillonite, has the ability to insert the organic molecules of essential oils into its structure, turning into organo bentonite and thus preserving the aroma of the oils for a longer time, preventing their degradation.

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***Authors' contributions**: The authors contributed equally to the study.*

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