Influence of the synthesis method on the preparation of immortelle oil microcapsules for cosmetotextiles

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Immortelle acts as an antibacterial and anti-inflammatory agent for hematomas, scars, eczema, skin infections and allergic reactions healing. Due to those benefits, immortelle essential oil was used as an active ingredient in microcapsule synthesis, while ethyl-cellulose (EC) was chosen for the wall material. Two synthesis techniques were compared: A - stirring method and B - ultrasonic method, with the aim to optimize microencapsulation process. Three different methods were used for the characterization: Dynamic light scattering (DLS) for the microcapsules in dispersed particle form; Confocal laser scanning microscope (CLSM) for synthesized microcapsules in dry state and Scanning electron microscopy (SEM) for the surface morphology of synthetized microcapsules applied to cellulose substrate (cosmetotextiles). DLS was also used to analyze zeta potential of synthetized microcapsules applied to cellulose substrate. All samples have shown the value of zeta potential within the range -37 and -47 mV, which indicates good stability of microcapsule suspension (i.e. repulsive forces prevail over attractive, thus preventing particles` aggregation) confirming good applicability for cosmetotextiles. Size of synthetized microcapsules proved to have influence on microcapsules effectiveness. In a case that active agent release rate needs to be increased the application of ultrasonic device is recommended for the synthesis, since it is resulting with smaller microcapsules of approx. 15 μm diameter which is considered as smaller size, easier for the application on textiles.
***Keywords**: immortelle oil, synthesis, microcapsules, cosmetotextiles.*

1. Introduction

In the forefront of various compounds for medical and skin-care purposes, immortelle (*Helichrysum italicum*) is becoming increasingly interesting due to its anti-inflammatory, antioxidant, antimicrobial, antiviral, skin-healing etc. activity [1-3]. Considering controlled drug delivery system preparation of microcapsules is one of the possible approaches [4]. Microcapsule is defined as a spherical particle with the size varying between 50 nm to 2 mm containing a core substance (e.g., ethyl-cellulose (EC)) and an active agent [4]. Above all, the size of the microcapsules is impor-

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tant, since smaller microcapsules are easier for application on textile material when compared to the larger ones [5]. Morphology, size, stability, and persistence of microcapsules depends on method of their preparation [4]. The mean size of microcapsules prepared by a spray-drying technique is usually between 4.1–4.7 μm. The size of microcapsules prepared by interfacial polymerization is approx. 13.35 μm while in the case of solvent-evaporation method is between 25–200 μm [6]. According to the literature, active agent release rate increases with the reduction of the particle size [6]. The aim of this research is preparation of immortelle oil microcapsules using stirring and ultrasound techniques and study the difference in their size, egality and zeta potential for the purpose of optimization of their effectiveness.

2. Materials and methods

2.1. Materials

Immortelle essential oil supplied by Croatian company Irex Aroma d.o.o. was used as an active component and ethyl cellulose (EC) (Sigma-Aldrich) as the wall material of microcapsules. To prepare microcapsules, the solvent-evaporation method described in Patent No.: US 6932984 B1 [7] was chosen [8]. The mass of immortelle oil in a separate treatment bath was 0.2 g. Additionally, oil-free microcapsules (0.0 g) were also prepared as a reference.

Two techniques were used for the microcapsule preparation:

A) Stirring method: Laboratory stirrer (Schott SLR, GmbH), 400 rpm, 10 min and

B) Ultrasound method: Vibra-CellTM Ultrasonic Liquid Processor VCX 500/VCX 750 controlled with On/Off pulser of ultrasound device enabling safe treatment of the temperature-sensitive samples at high intensity thus providing uniform mixing allowing the sample to settle back under the probe after each burst [9]. On/Off Pulser (2 s on/ 1 s off) provided amplitude of 60 %. Time of ultrasound treatment was 5 min. Additionally; ice was used to adjust and stabilize temperature during the preparation.

Cotton samples (20 x 20 cm) in a plain weave and surface mass of 90.9 g/m^2 with the warp/weft yarn density of 52/43 yarns/cm were applied. Samples were treated with 15 mL of EC microcapsules having 0.0 and 0.2 g of immortelle oil added to 200 mL of deionized water, together with the 0.3 g of anionic surfactant (sodium dodecyl sulphate (SDS), Fluka) and 1 g of fixation agent (Helizarin Binder TW, BASF). The conventional pad-dry process at foulard W. Mathis with wet pick-up of approx. 100% was used to apply microcapsules onto cotton samples. Treated samples were dried at ambient temperature and prepared for further analysis.

2.2. Methods

EC microcapsules were evaluated with three different techniques: 1.) Dynamic Light Scattering (DLS); 2.) Confocal Laser Scanning Microscopy (CLSM) and 3.) Scanning Electron Microscopy (SEM).

DLS method was used to determine the size distribution profile of the microcapsules in a suspension, so as the zeta-potential which is is often used as a metric to determine the particles' stability in the colloidal sense [10]. By using Zetasizer Nano ZS (Malvern, Worcestershire) it is possible to analyze the particles of a maximum dimension of 10 μm, so the size of prepared microcapsules (method A and B) was determined using three replicates under the ambient temperature.

Confocal laser scanning microscope Leica TCS SP5 II, equipped with a LAS AF imaging software (Leica Microsystems), was used for qualitative analyses of microcapsules. Prior to the CLSM analysis, microcapsules were dyed with the fluorescein isothiocyanate isomer I (90 %, HPLC, Sigma Aldrich) with characteristic wavelengths λ_{max} for excitation is 490 nm and for emission is 525 nm measured in a dry state.

Scanning Electron Microscope (MIRA\FE-SEM, Tescan) was used for surface characterization of microcapsules applied on fabric under the magnification of 1000x to 5000x, using accelerating voltage of 10.00 kV. Prior to measurement, samples were sputter-coated with palladium/gold alloy.

Add-on of the EC microcapsules and binder (i.e. the difference in the mass of the treated sample in comparison to the untreated one) was determined at cotton cosmetotextiles using gravimetric method.

3. Results

3.1. Evaluation of EC microcapsules in polydisperse system using DLS technique

Variation of microcapsules' size as a function of amount of added oil and the type of preparation was highlighted through DLS measurements. Table 1 shows results of DLS (the size, the polydispersity (PdI) index and zeta potential) of microcapsules synthetized by stirring (A) and ultrasonic (B) methods in dependence on the mass of the added immortelle oil.

Results show that amount of oil used in preparation has significant influence on the size of particles. The results of reference sample (0.0 g) revealed significant difference in dimensions dependant on the method of preparation. Procedure A (stirring) resulted with

Tab.1 Characteristics of synthetized microcapsules by DLS

	Stirring method (A)			Ultrasonic method (B)		
Mass of oil (g)	Size (nm)	Index of polydispersity Pdl	Zeta potential (mV)	Size (nm)	Index of polydispersity Pdl	Zeta potential (mV)
0.0	1978.0	0.641	-43.4	794.52	0.620	-47.1
0.2	3161.1	0.908	-44.7	217..03	0.504	-37.3

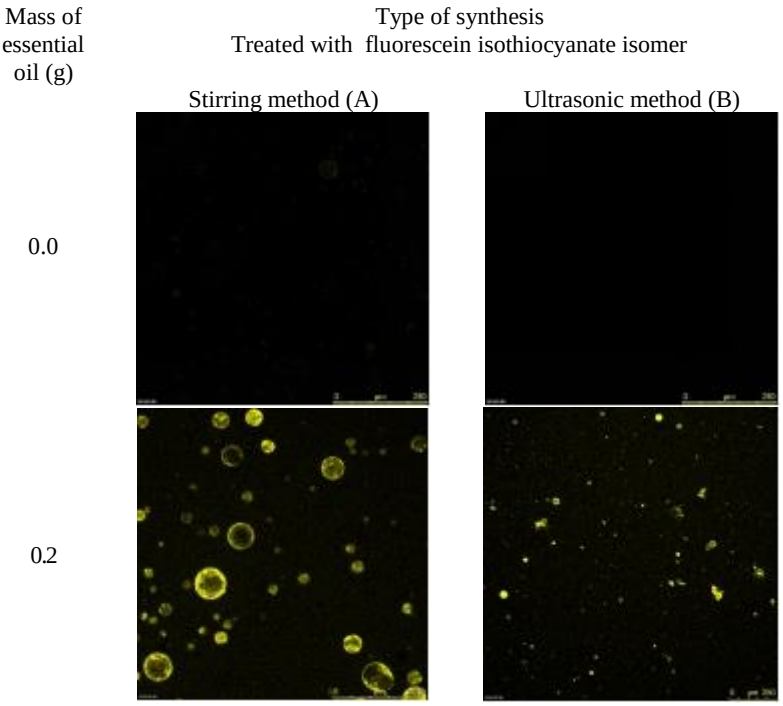

Fig.1 Confocal microscope scans (magnification 250x) of microcapsules with oil (0.2) and without oil (0.0), by using two different procedures of synthesis: A (stirring) and B (ultrasonic)

Tab.2 Gravimetric analysis of cotton fabric functionalized with microcapsules synthetized by methods A and B

Microcapsules Synthesis	Mass of added immortelle oil (g)	Δm x 10^{-2} (g)
Method A	0.0	1.12
	0.2	3.69
Method B	0.0	1.25
	0.2	4.00

microcapsules of average size 1978.0 nm while with procedure B (ultrasonic) much smaller size (794.52 nm) was obtained. The same is with the addition of 0.2 g of oil; in procedure A microcapsules average size was 3161.1 nm while in procedure B average size of microcapsules was decreased to 2178.03 nm.

Index of polydispersity (Pdl) with the procedure B is lower than 0.7 indicating that the samples have relatively narrow size distribution. Only in the case of procedure A when 0.2 g of oil was added Pdl value (e.g., 0.908) was too high. All samples show the value of zeta potential (Tab.1) within the range -37.3 and -47.1 mV, which indicates hydrophobic surface and good stability of microcapsules suspension i.e., repulsive forces prevail over attractive, thus preventing particles` aggregation.

3.2. Evaluation of dry microcapsules using CLSM technique

Synthesized microcapsules were coloured with the Fluorescein isothiocyanate isomer (FII). Coloured microcapsules, either without (0.0) or with the 0.2 g of oil were analysed with confocal laser scanning microscope (CLSM), (Fig.1). Obtained results confirmed the influence of synthesis method on microcapsule size. Microcapsules synthetized with the method A are in the size range of 10-100 μm and microcapsules synthetized with the B method are in the smaller size range of 1-40 μm. Microcapsules synthesized under the procedure B in polydisperse system have approx. 10 times smaller size if compared to microcapsules synthesised under the procedure A. Oil microcapsules (A 0.2 and B 0.2) scanned with fluorescence have yellow dyed parts, on the other hand microcapsules without oil (A 0.0 and B 0.0) have undyed parts because the oil is not part of the functionalization system. CLSM combined with fluorescence dyeing pre-treatment confirmed the presence of oil within microcapsules.

Surface of functionalized cotton fabrics was investigated by the SEM analysis under different magnifications (1000x and 5000x) and presented at Figs.2 and 3. Presence of EC microcapsules, their distribution, uniformity, shape and size were analyzed at all functionalized cotton samples.

SEM micrographs of functionalized cotton samples confirmed the presence of EC microcapsules on the surface. The synthesized microcapsules revealed regular oval shape and different size, depending on the synthesized method. Microcapsules syntheticzed using stirring method (A) investigated at the textile surface are in the size range of 10-60 μm with an average diameter of approx. 45 μm. Microcapsules synthetized using ultrasonic device (B) are in the size range of 10-20 μm with an average diameter of approx. 15 μm.

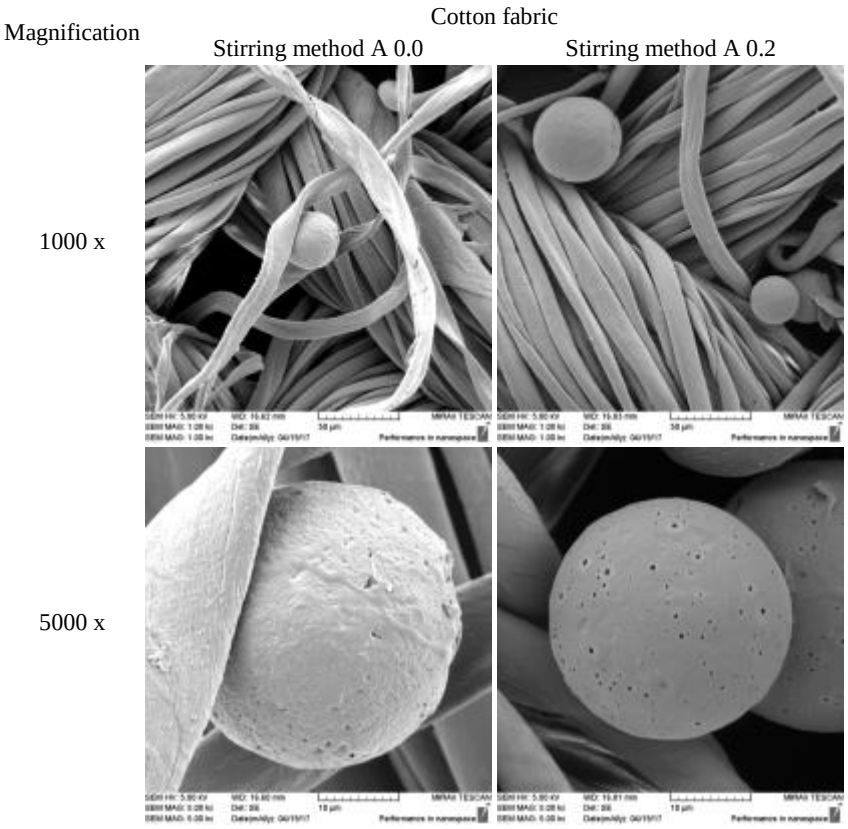

Fig.2 SEM micrographs of cotton fabric functionalized with EC microcapsules synthetized by stirring method (A) with different mass of immortelle oil:
a) 0.0 g; b) 0.2 g

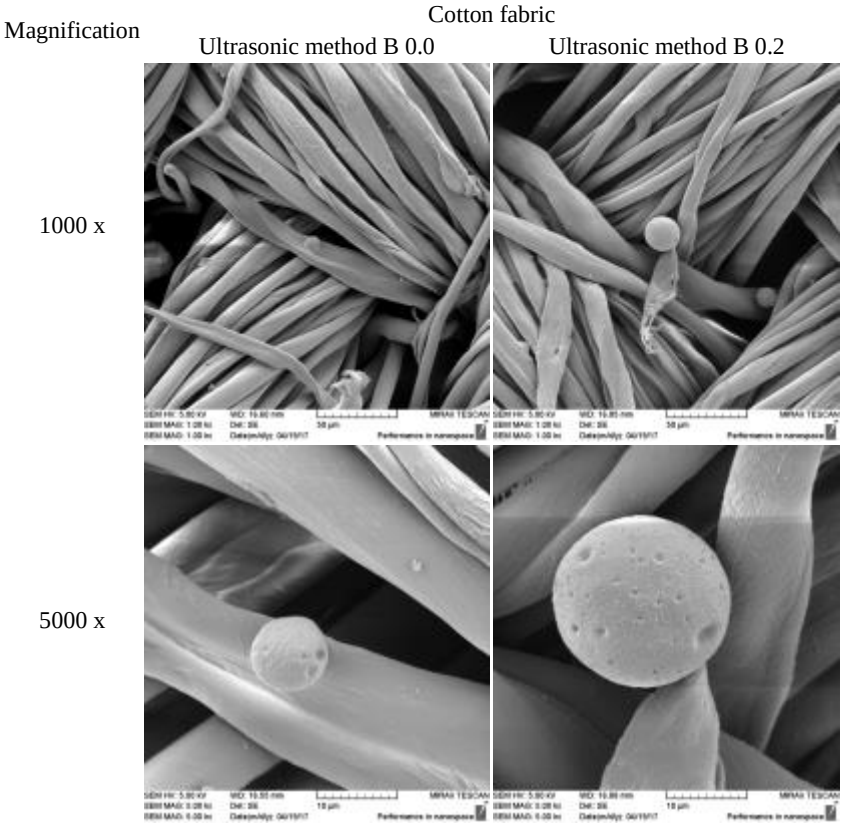

Fig.3 SEM micrographs of cotton fabrics functionalized with EC microcapsules synthetized by ultrasonic method with different mass of immortelle oil (B):
a) 0.0 g; b) 0.2 g

SEM proved to be efficient tool to determine the size of dry microcapsules applied at the textile surface and therefore to differentiate between two methods of synthesis used within this research.

4. Conclusions

DLS method used for particle size analysis up to 10 μm is very fast method but it should be combined with SEM analysis.

Confocal microscopy is convenient method for determination a presence of oil in microcapsules.

Gravimetric analysis confirmed effectiveness of functionalization with microcapsules. It is noticeable that fabric mass after the functionalization with EC-oil microcapsules is higher for approx. 3.8 g compared to the EC microcapsules without oil.

Microcapsules type of synthesis should be chosen depending on the usage of cosmetotextiles.

In a case that active agent release rate needs to be increased the application of ultrasonic device method is recommended for the synthesis. Application of stirring as synthesis method results with microcapsules of average 45 μm diameter while application of ultrasonic device method results with smaller microcapsules of average 15μm diameter.

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