Preparation of microcapsule for citriodiol controled release

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The purpose of the research was the preparation of environmentally friendly ethyl cellulose micro-particles encapsulating citriodiol as model volatile compound. Microcapsules were synthesized by homogenizing the organic solution (ethylcellulose, ethylacetate, citriodiol) and aqueous solution with surfactant. The resulting microcapsules were characterized by the determination of the polydispersity index, the particle size distribution, the zeta potential and microscopic observations. The size of the resulting microcapsules strongly depended on the method of stirring while adding the organic solution into the aqueous solution. It was found that the microcapsules must be prepared using homogenizer in order to gain uniform shapes. The polydispersity index determination confirmed that homogenization enables midrange monodispersed sample. If magnetic stirrer was used the microcapsules' size distribution was broader. The zeta potential measured around - 40 mV confirmed stable microcapsules. The ATR FTIR spectra of citriodiol, ethyl cellulose and the resulting micro capsules were also studied. As well as by microscopic measurements the presence of the active component captured inside the microcapsules was confirmed. In the future work the appropriate control method of the citriodiol release from microcapsules has to be provided.
Keywords: *microcapsule, citriodiole, ethylcellulose, controlled release*

1. Introduction

Encapsulation can be performed by means of different techniques to obtain micro and nanosystems. Particles are surrounded by a wall to form small capsules [1, 2]. The main advantage of pesticide encapsulation is the solid state of product, which is easier to apply [2]. Aqueous dispersion is very convenient for controlled release technique of compound, such as pesticide at recommended rates. Bio-derived repellents are interesting for pest control due to their environmental friendly nature [3]. Citriodiol is the most effective bio-repellent against a range of biting insects, nuisance insects and ticks. It has been included in the European Biocidal Products Directive (BPD) 98/8/EC.

Microencapsulation is a method in which tiny particles or droplets are surrounded by a coating wall. Size and shape of the formed microcapsules depend on wall materials and the methods used to prepare them. Commonly used microencapsulation techniques are: emulsification, spray-drying, coaxial electrospray system, freeze-drying, coacervation, *in situ* poly-

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merization, extrusion, fluidized-bedcoating, and supercritical fluid technology [2].

Controlled release technology is used to deliver various compounds such as drugs, pesticides, fragrances, or flavours at recommended rates, together with improved efficacy and safety [4].

The aim of the research was the preparation of eco-friendly ethyl cellulose microcapsules entrapped with citriodiol as model volatile compound. Core-enriched nanofibers were prepared using a coaxial nozzle, recently. In present research microcapsules were synthesized by homogenisation of the organic solution (ethyl cellulose, ethyl acetate, citriodiol) and aqueous solution with surfactant. The resulting microcapsules were characterized by the determination of the polydispersity indeks (PDI), the particle size distribution, the zeta potential and microscopic observations.

2. Experimental

2.1. Materials

Citriodiol is an extract of *Myrtaceae* leaves. It consists of 64% of p-methane-3,8-diol (PMD), with traces of citrionellol, acethal, etc. At room temperature citriodiol is yellow viscous liquid with white crystals (Fig.1).

Fig.1 Citriodiol drop

At 50ºC crystals melt and homogenous yellow liquid forms. Boiling point is 267ºC and is soluble in water 670.7 mg/L.

Citric Acid, ethyl acetate and ethyl cellulose were purchased from Sigma-Aldrich and Sodium dodecyl sulfonate from Fluka.

2.2. Microcapsule preparation

In 25 mL flask 0.6 g of ethyl cellulose was weighted and 15 mL of ethyl acetate was added. The mixture was mixed on magnetic stirrer for 8 min and then 0.25 mL of citriodiol was added at 60 ºC and mixed for 10 min to gain liquid state of citriodiol. In 400 mL jar 1 g of SDs was dissolved in 100 mL a. d. and 10 mL of ethyl acetate. pH was adjusted to 3 using citric acid. The organic phase was poured into water phase and mixed homogenised using IKA T18 Basic at 11 000 rpm for 4 min. 200 mL a. d. was added. The prepared samples were centrifuged for 5 min at 5000 rpm.

2.3. Microcapsule characterisation

Microscope was used for observation of formed microcapsules.

The size of microcapsules was determined using zetasizer Nano ZS. Dynamic light scattering technique was applied for measuring size. Zeta potential was measured by electrophoretic mobility at the same device.

ATR FT-IR spectra were recorded on a Perkin Elmer Spectrum GX spectrometer in wavelength interval between 4 000 and 650 cm^{-1}.

UV/VIS spectrophotometer was used for measuring the concentration of citriodiol. The maximum absorbency of citriodiol was determined at 273 nm, while ethyl cellulose at 253 nm.

3. Results and Discussion

After centrifugation the filtration was needed to separate supernatant from capsule, which were in solid state and dried at room temperature. The microcapsules can be seen in Fig.2.

Fig.2 Prepared microcapsules

The microcapsules can be seen as brown particles under microscope, Fig.3. 400x magnification (Fig.3 right) shows that microcapsules are formed in very different sizes, mostly as spheres.

In Tab.1 the particle size is shown and PDI. The size is above 10 µm if homogenisation was not applied as seen from Tab.1, samples No 1, 2 and 3. The particle size is smaller and more unified with homogenization as seen from Tab.1, samples No 4 and 5. PDI differs a lot. It shows the heterogeneous population with very large deviation in particle size and shape. It is in correspondence with microscopic observations.

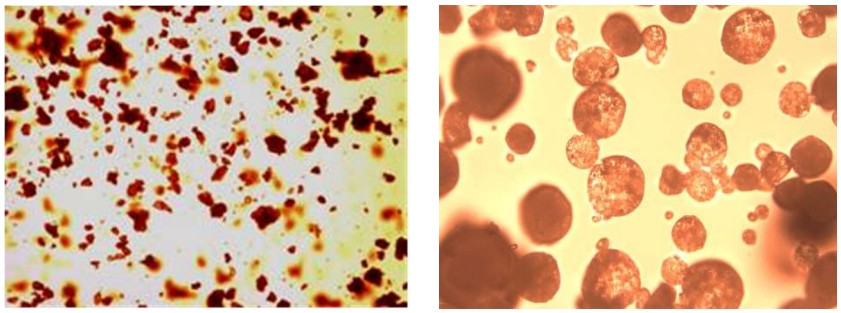

Fig.3 Microcapsules under microscope (right - 400x magnification)

Tab.1 Sample diameter (d) and poly-disperse index (PDI)

Sample No	d [µm]	Average d MK	PDI	Average PDI
1	13.68		0.809	
	10.62	13.78	0.353	0.455
	17.05		0.203	
2	10.18		0.242	
	15.95	13.08	0.302	0.442
	13.11		0.783	
3	15.44		0.773	
	9.312	11.76	0.587	0.649
	10.53		0.587	
4	1.388		0.259	
	1.384	1.41	0.37	0.445
	1.465		0.708	
5	2.03		0.187	
	1.08	1.63	0.763	0.588
	1.772		0.814	

Tab.2 Sample zeta potential measurements (ζ)

Sample	ζ [mV]	Average ζ [mV]
1	-49	
	-46	-46.2
	-43.6	
2	-32	
	-37.8	-36.1
	-38.5	
3	-36.2	
	-46.7	-41.5
	-41.6	
4	-42.2	
	-41.8	-41.96
	-41.9	
5	-41.9	
	-39.7	-40.7
	-40.5	

Tab.2 shows the zeta potential measurements. The zeta potential measurements showed the stable disperse system. Measurements showed the zeta potential around -40 mV which indicates stable solution [5]. If microcapsules were prepared by homogenisation, the zeta potential was in range 41 ± 1 mV, while larger deviation (± 5 mV) was observed in samples which were prepared by stirring with magnetic stirrer.

3.1. ATR FTIR spectra

Fig.4 represents ATR FTIR spectra of ethyl cellulose (A), citriodiol (B) and microcapsule (C).

In ATR FTIR spectrum of ethyl cellulose signal at 3400 cm^{-1} represents vibrational O-H stretching and signals between 2700 cm^{-1} and 2860 cm^{-1} as well as 1375 cm^{-1} represent C-H bending.

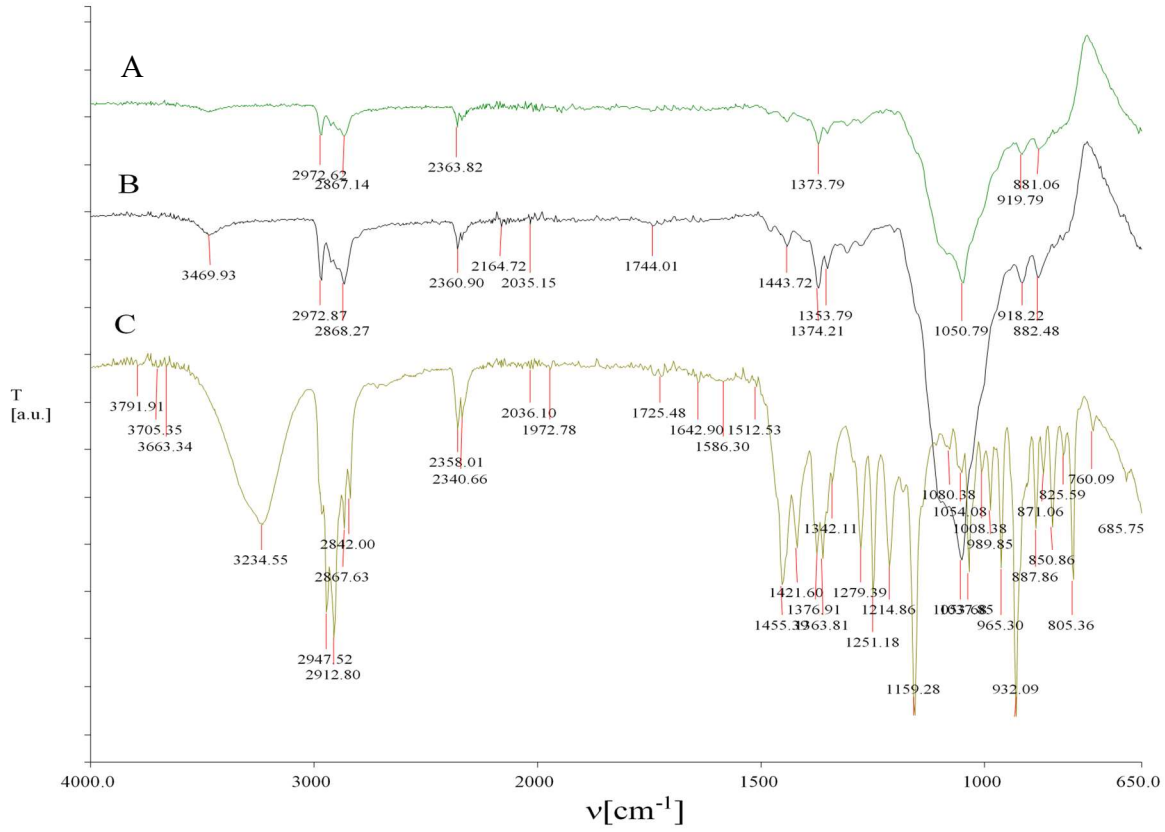

Fig.4 ATR FTIR spectra of ethyl cellulose (A), citriodiol (B) and microcapsule (C)

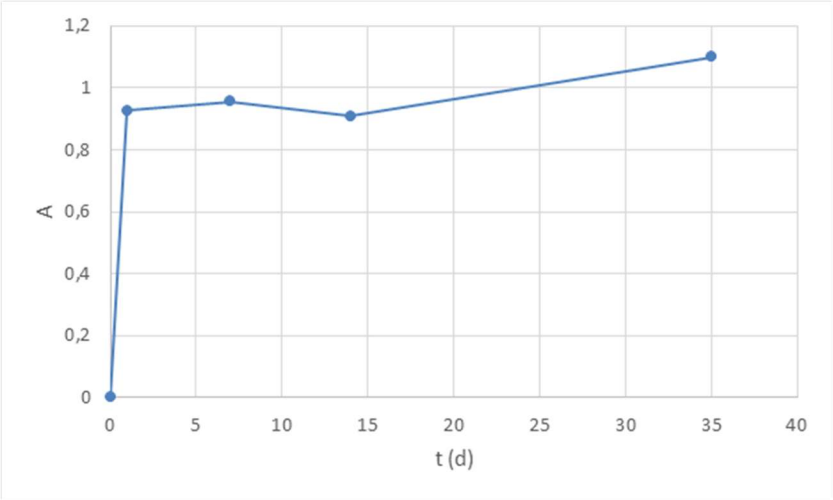

Fig.5 Release control of citriodiol

Signal at 1100 cm^{-1} represents C-O vibrations. ATR FTIR spectrum of citriodiol represent typical signals at 1455, 1251, 1155, 932 and 805 cm^{-1}.
ATR FTIR spectrum of microcapsule shows characteristic fingerprint signals of ethyl cellulose (A) Such result was expected since ATR FTIR technique measures surface properties (penetration depth of around 1 or 2 μm).
Fig.5 represents the release of citriodiol from microcapsule. It is seen that concentration is still increasing after 15 days. It was proposed that all citriodiol would be released after a month according to literature data for ethyl vaniline [1], however, Fig.5 shows that it is still present after 35 days. It should be measured after longer periods.

4. Conclusion

Microcapsule with entrapped citriodiol were prepared. The size of the resulting microcapsules strongly depended on the method of stirring while adding the organic solution into the aqueous solution. It was found that the microcapsules must be prepared using homogenisation in order to gain uniform shapes. The polydispersity index determination confirmed that homogenisation enables midrange monodispersed sample. If magnetic stirrer was used the microcapsules' size distribution was broader. The zeta potential measured around -40 mV confirmed stable microcapsules.
The ATR FTIR spectra of citriodiol, ethyl cellulose and the resulting microcapsules were also studied. The presence of the active component captured inside the microcapsules was confirmed matching the microscopic measurements.

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