

Sustainable Microencapsulation of Limonene via Complex Coacervation with Natural Biopolymers

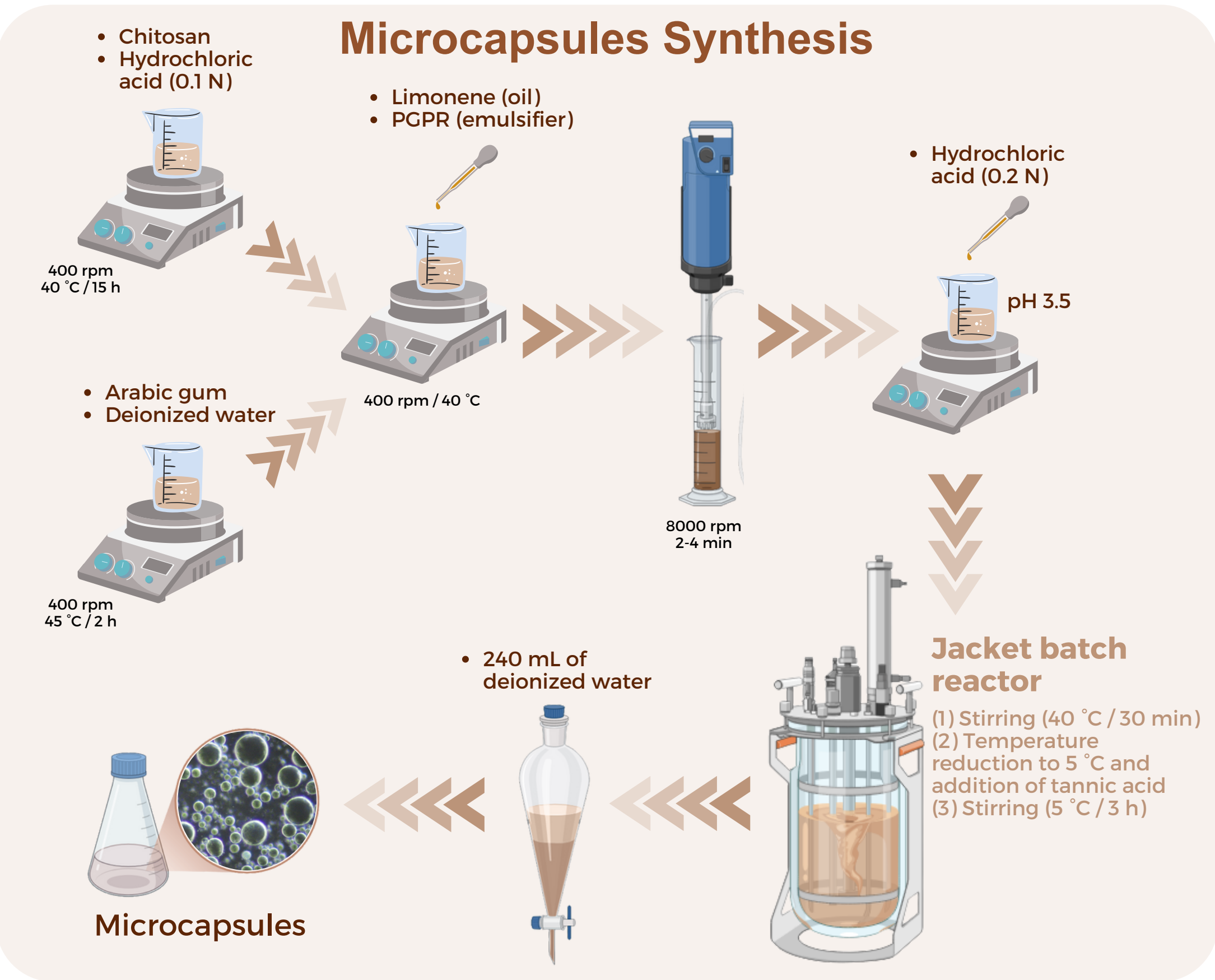
Guilherme Andreoli Gil¹, Maria Filomena Barreiro², Caroline Casagrande Sipoli¹, Isabel Patrícia Martins Fernandes³, Fabricio Maestá Bezerra⁴
¹guilherme_gil_@hotmail.com

¹ Department of Chemistry Engineering, Federal University of Technology—Paraná (UTFPR), 635 Marçílio Dias St., 86812-460 Apucarana, Paraná, Brazil
² School of Technology and Management of the Polytechnic Institute of Bragança (ESTiG-IPB), Santa Apolónia Campus, 5300-253 Bragança, Portugal
³ Research and Development Department, Tree Flowers Solutions, Brigantia EcoPark, 506 Cidade de León Ave., Lab. 213, 5300-358 Bragança, Portugal
⁴ Department of Textile Engineering, Federal University of Technology – Paraná (UTFPR), 635 Marçílio Dias St., 86812-460 Apucarana, Paraná, Brazil

INTRODUCTION & OBJETIVES

Essential oils have been widely explored in various industrial sectors due to their bioactive properties and health benefits. Among their main constituents, terpenes stand out, with limonene being one of the most abundant in nature, especially present in citrus essential oils. This compound exhibits well-recognized antioxidant, antimicrobial, aromatic, and therapeutic activities, making it highly attractive for applications in the pharmaceutical, cosmetic, food, and sustainable materials industries. However, its high volatility and sensitivity to adverse environmental conditions limit its stability and direct application in formulations. To overcome these limitations, microencapsulation emerges as an efficient strategy to preserve the functional properties of limonene and enable its controlled release. In this study, natural biopolymers such as chitosan and gum arabic were used to produce limonene microcapsules through complex coacervation, a sustainable and versatile encapsulation technique. The objective of this work was to investigate the effect of biopolymer concentration and limonene content on the productivity and properties of the microcapsules, as well as to evaluate the feasibility of the process as a sustainable approach for the protection and controlled release of bioactive compounds.

METHOD



Limonene microcapsules were produced by complex coacervation using chitosan and gum arabic as wall-forming biopolymers. Aqueous solutions of chitosan and gum arabic were prepared under stirring and heating until complete dissolution. The solutions were then mixed at 40 °C, followed by the addition of limonene and the emulsifier (PGPR). The emulsion was formed by mechanical homogenization at 8000 rpm using an Ultraturrax. The pH of the mixture was adjusted to 3.5 to promote electrostatic interactions between the biopolymers. The dispersion was maintained under stirring at 40 °C for 30 minutes and then cooled to 5 °C to induce complex coacervation. A tannic acid solution was added dropwise to harden the microcapsule walls. Finally, the microcapsules were recovered by decantation and washed with deionized water. Four different formulations were produced, varying specific parameters, as presented in Table 1. The obtained microcapsules were characterized by optical microscopy for morphological analysis, gravimetric analysis for solid content, laser diffraction for particle size, and gas chromatography (GC-FID) for encapsulation efficiency determination.

Table 1 - Formulations used for microcapsule production.

Assay	Chitosan solution concentration (% w/v)	Gum arabic solution concentration (% w/v)	Limonene mass (g)	Emulsifier mass (g)	Volume of tannic acid solution (mL)
1	1	2	9	1.2	4
2	2	4	9	1.2	4
3	2	4	18	2.4	8
4	2	4	27	3.6	8

RESULTS & DISCUSSION

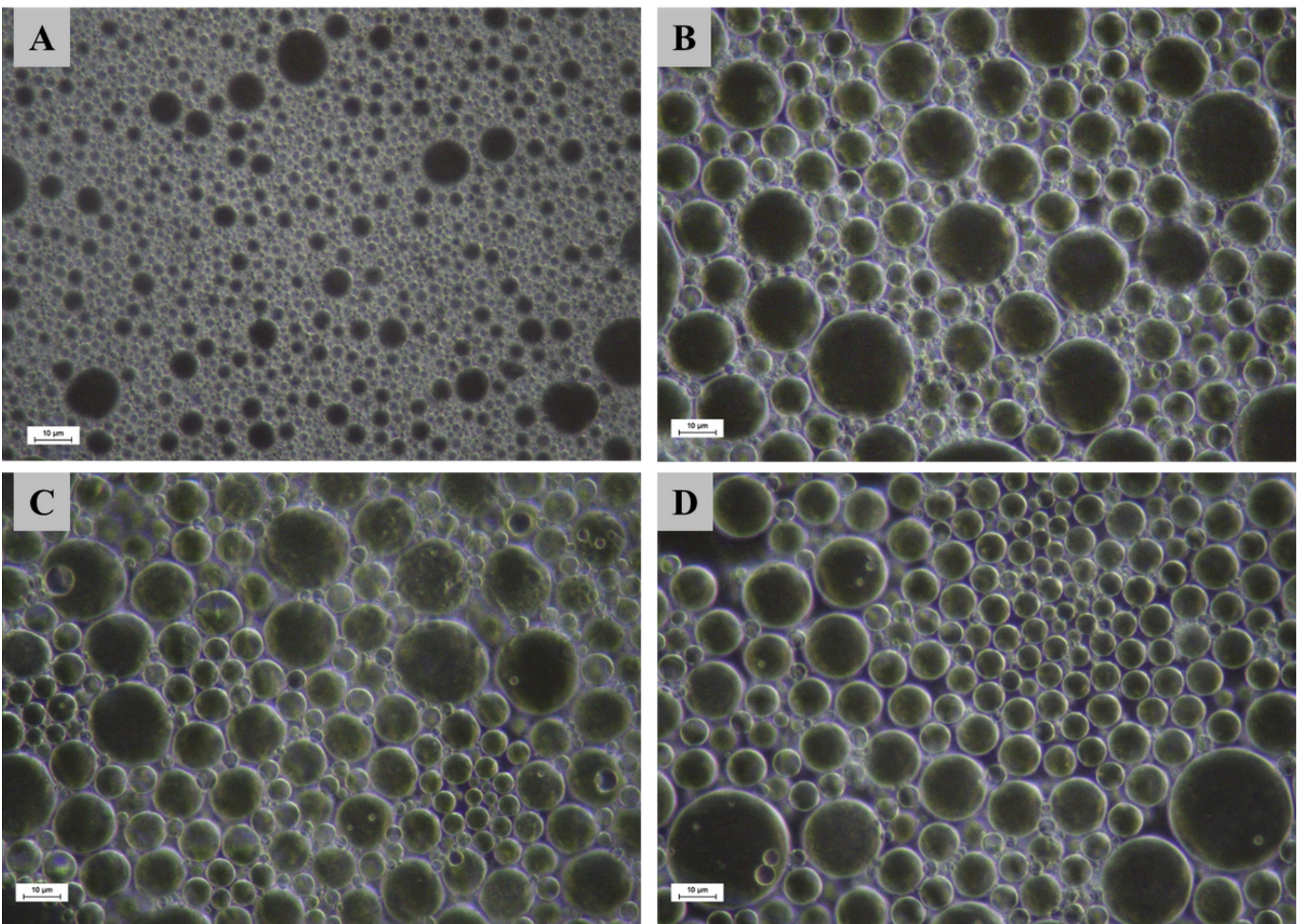


Figure 1 - Optical microscopy of the microcapsule samples from assays 1, 2, 3, and 4 (A, B, C, and D, respectively) (magnification 400×).

Table 2 - Solid content, particle size, and encapsulation efficiency of limonene microcapsules obtained by complex coacervation.

Assay	Experimental solid content (% w/w)	Theoretical solid content (% w/w)	Particle size Before the washing (µm)	Particle size After the washing (µm)	Encapsulation Efficiency (%)
1	2.06	5.81	1.12	0.74	-
2	5.68	7.09	1.22	0.96	99.5
3	4.06	11.43	1.00	1.01	99.2
4	4.35	15.08	0.97	0.93	99.7

Optical microscopy analysis showed that all formulations produced regular and consistent particles with predominantly spherical and uniform morphology, presenting diameters between 1 and 10 µm. The solid content of the microcapsules ranged from 2.06% to 5.68% (w/w), values close to the theoretical ones calculated based on the raw materials used. Increasing the concentrations of limonene and emulsifier did not result in a significant increase in solid content, possibly due to the low oil content in the system. The average particle size ranged from 0.74 to 1.22 µm. Variations in biopolymer concentration and limonene mass altered the core-to-wall ratio but did not significantly affect the average size of the formed microcapsules. The encapsulation efficiencies were extremely high, above 99% in all samples, indicating that the biopolymer concentrations used were sufficient to ensure complete encapsulation of the available oil. These results confirm the efficiency of the process and suggest that the system still has the capacity to incorporate larger amounts of core material, thereby increasing productivity and the encapsulated load.

CONCLUSION

The results demonstrate that complex coacervation using natural biopolymers is a sustainable, versatile, and efficient technique for the microencapsulation of limonene. Therefore, the study highlights the potential application of these microcapsules in high-value and innovative formulations across various industrial sectors, including pharmaceuticals, cosmetics, food products, and sustainable materials.

FUTURE WORK & REFERENCES

Future work will focus on studying the antioxidant and antimicrobial activities of limonene, as well as on the structural and chemical characterization (FTIR-ATR) and thermal stability evaluation of the microcapsules.

[1] BARBOSA-NUÑEZ, J. A. et al. *Journal of Future Foods*, v. 5, n. 1, p. 36-49, 2025
[2] TARIQ, H. et al. *Polymer Bulletin*, v. 81, p. 7585–7629, 2024
[3] SHARKAWY, A. et al. *Industrial & Engineering Chemistry Research*, v. 56, p. 5516–5526, 2017
[4] MATOS, E. F. et al. *Journal of Environmental Chemical Engineering*, v. 6, p. 1989–1994, 2018