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"Development of a technological Eco-Friendly platform for the Nanoencapsulation of Fragrances "

ABSTRACT

The increasing demand for sustainable, high-performance cosmetic formulations has prompted the development of novel encapsulation technologies for volatile compounds such as fragrances. This study introduces an innovative, eco-friendly encapsulation platform strategy based on a combination of Phase Inversion Composition (PIC) low-energy emulsification and alginate microgel formation. The approach enables the stable incorporation of fragrance nanoemulsions into biodegradable sodium alginate matrices, ensuring enhanced fragrance retention and controlled release without reliance on non-biodegradable synthetic polymers. Nanoemulsions were formulated via a PIC method using ethyl acetate–hexane oil phases and polysorbate 80 as a surfactant, achieving high monodispersity and stability with minimal mechanical energy input. Following optimization, fragrance-loaded nanoemulsions were encapsulated within calcium-crosslinked alginate microgels via mild ionic gelation. To enable characterization of this newly developed capsule library, a robust GC-MS method was established to quantify the system's encapsulation efficiency. The method was validated using a model fragrance, which demonstrated an encapsulation efficiency exceeding 80%, confirming the suitability of the approach for complex formulations.This dual technological platform—combining spontaneous nanoemulsion formation with biodegradable biopolymer encapsulation—addresses key challenges in fragrance stabilization and release kinetics while aligning with evolving environmental and regulatory standards. The method demonstrates scalability, regulatory compliance, and strong potential for future cosmetic applications focused on eco-responsible innovation.

1. Introduction

Fragrances play a key role in cosmetics and personal care products, as they contribute to product identity and play an important role in consumers' emotional experience during use [1]. However, the intrinsic volatility of fragrance compounds often results in a rapid loss of scent after application, reducing long-term effectiveness and consumer satisfaction. To overcome these limitations, encapsulation technologies have been widely used to protect fragrances from environmental factors degradation, such as light, oxidation agents, or temperature variations, and to control their release profiles [2].

Traditional encapsulation methods have largely relied on synthetic polymer matrices or acrylates, many of which are non-biodegradable and contribute to environmental concerns such as microplastic pollution [3,4]. Regulatory organizations, including the European Chemicals Agency (ECHA) and the International Fragrance Association (IFRA), are increasingly

restricting the use of persistent synthetic materials, particularly in rinse-off applications, to mitigate their ecological impact [5,6,7]. These developments have driven a growing need for sustainable encapsulation strategies that align with the principles of environmental responsibility and green chemistry. Additionally, the trend towards ‘green’ cosmetics and the growing ecological awareness of the consumer reinforce this need.

Sustainable alternatives include cyclodextrins, PLGA (polyacid lactic-co-glycolic acid), liposomes, chitosan, gum arabic, alginates, or other polysaccharides. These materials offer the biodegradability and biological compatibility necessary to reduce environmental impact. However, these substitutes often present challenges such as low encapsulation yields, too rapid release of fragrance, high production costs or a combination of these factors. These limitations hinder their scalability and industrial implementation [2,8,9].

A further difficulty in encapsulating fragrances is due to their complex physico-chemical nature. Fragrances are mixtures of aromatic molecules, with significant differences in polarity, viscosity and density. This means that encapsulation using traditional emulsification techniques, often based on the use of different surfactants, is not optimal for highly polar compounds. Furthermore, the migration of small molecules through the continuous phase (Ostwald ripening), leads to premature destabilisation of emulsions.

In response to these challenges, we have developed an innovative and sustainable encapsulation platform strategy based on a fragrance nanoemulsion encapsulated in a alginate matrix. Specifically, we have opted for the encapsulation of fragments in a polynuclear encapsulation system using a low-energy method. The system used combines the formation of nanoemulsions by phase inversion (the PIC method) with the subsequent gelation of this nanoemulsion in a sodium alginate matrix.

The formation of nanoemulsions using the PIC method has several advantages over other conventional high-energy methods, such as lower energy consumption and stable emulsions without the need for intense mechanical inputs [10,11,12,13]. This process takes advantage of the spontaneous curvature changes of surfactants (such as polysorbate 80) during the progressive addition of the continuum, forming lamellar structures and later emulsions, in this case O/W, with high monodispersity.

The PIC method offers a versatile approach for developing stable nanoemulsion-based delivery systems by enabling precise control over formulation parameters. Through systematic evaluation of key factors, this method allows the creation of a flexible platform capable of generating diverse capsule compositions. To further enhance stability, the resulting nanoemulsions are encapsulated within a calcium cross-linked alginate matrix, forming a semi-permeable barrier. In this system, the release of the encapsulated phase is primarily governed by the intrinsic stability of the nanoemulsion.The primary objective of this research is to develop and characterize physico-chemically and organoleptically, a biodegradable, scalable fragrance encapsulation platform that complies with current regulatory and environmental requirements while maintaining high performance in terms of fragrance stability and release. This work addresses critical gaps in sustainable formulation technologies and aims to contribute a viable solution for the future of eco-friendly cosmetic product development.

2. Materials and Methods

2.1. Materials

Phosphate Buffered Saline (PBS) 10X solution (1.37 M sodium chloride, 0.018 M potassium dihydrogen phosphate, and 0.027 M potassium chloride and 0.1 M disodium phosphate at pH of 7.4 was purchased from Lonza. All experiments were performed using MilliQ® filtered grade water (resistivity of 17.1 mΩ·cm; surface tension = 72.8 mN/m). NaCl extra pure and Glycine of purity 99% was supplied from Scharlau. Ethyl Acetate and Hexane are supplied from VWR chemicals. Polysorbate 80 (Tween 80®, HLB = 15), $CaCl_2$ dihydrate of purity 99%, Sodium Alginate (SA) medium viscosity, Nile Red dye was purchased by Sigma-Aldrich. Hydrochloric acid 37% was purchased from PanReac. Reference Fragrance (logP of 3.32) was provided by collaboration company.

2.2. Methods

2.2.1. Preparation of sodium alginate (SA)-Fragrance Microencapsulated system

Sodium alginate microcapsules (SA-MC) containing an internal oil-in-water nanoemulsion (O/W NE) were prepared using a phase inversion composition (PIC) method. This low-energy emulsification technique was followed by the internal gelation of sodium alginate and subsequent dispersion to form non-spherical SA-MC structures.

Polysorbate 80 was used as the surfactant to prepare the O/W nanoemulsion. It was first homogenized with the fragrance oil to form the oil phase. The aqueous phase (Milli-Q® water) was then added dropwise while continuously stirring at 3000 rpm using a Velp Scientifica ZX4 vortex mixer. The surfactant-to-oil and oil-to-water ratios were adjusted according to the specific experimental parameters.

After the nanoemulsion was formed, sodium alginate (medium viscosity) was added to the system to achieve a final concentration of 1% w/v. The nanoemulsion was subsequently added dropwise to a 1% (w/v) calcium chloride ($CaCl_2$) solution to initiate the internal gelation of the alginate.

Finally, the SA nanoemulsion gel was dispersed at high shear for 3 minutes at 25,000 rpm resulting in the formation of the final non-spherical sodium alginate–fragrance microcapsules (SA-MC).

2.2.2. Hydrodynamic diameter, polydispersity index determination of NE

Measurements were performed by DLS (ZetaSizer Nano ZS, from Malvern Instruments Ltd, United Kingdom equipped with a 4mW He-Ne red light laser using a laser wavelength of 633nm. The detector is placed at angle of 173 degrees to the sample). Hydrodynamic diameter and PDI were determined with an undiluted sample (200 µL) in 1 cm x 1cm polystyrene cuvette. The measurements were performed thrice with 10 runs per measurement at 25°C with 30 seconds of equilibrium time. Data was treated by cumulant and CONTIN analysis to obtain hydrodynamic size.

2.2.3. Encapsulation efficiency determination by Gas Chromatography coupled to a Mass Spectrometry detector (GC-MS)

The analysis was performed using an Agilent 5977A GC/MSD system coupled with a Mass Selective Detector (MSD), operating in scan mode with a mass range of 50 to 550 m/z. Chromatographic separation was achieved using a nonpolar Agilent HP5ms column (30 m x 0.250 mm, 0.25 µm), with helium as the carrier gas at a constant flow rate of 1.2 mL/min. The

temperature program began at 50°C, with a 15°C/min ramp to 270°C, followed by a 5-minute hold. The system was controlled with Agilent OpenLab CDS software.

The chromatographic profile of the fragrances was first determined at 70°C, 90°C, 130°C, and 180°C to identify the most important fragrance compounds and their chromatographic profile. The sample was characterized by analyzing the total fragrance loaded into the capsules and the residual fragrance. Encapsulation efficiency was calculated based on normalized peak areas of the compounds. All experiments were conducted in triplicate, with a method blank and empty capsule prepared to ensure that no extraneous peaks were present.

2.2.4 Statistical analyses

Statistical analysis was generally performed using ANOVA and descriptive statistics. Unless otherwise specified, all experiments were conducted with a minimum of three replicates. Results are presented as mean values ± standard deviation. A Student's t-test was used to assess statistical differences between samples. Differences were considered statistically significant when the p-value from the analysis of variance was less than 0.05.

3. Results

The formation of nanoemulsions (NE) using the Phase Inversion Composition (PIC) technique allowed the obtaining of stable emulsions of controlled size. The effectiveness of the PIC method is directly influenced by the polarity of the oil phase, the surfactant and aqueous phase ratio and additionally, how the aqueous phase is added to the oily phase. To establish a robust formulation for encapsulating fragrances, studies to stablish the robust and versatile platform for fragances encapsulation were performed using model oil phases with varying polarity. These emulsions,prepared by Phase Inversion Composition (PIC) method, uses polisorbate 80 as a non-ionic surfactant and maintaining 90% of aqueous phase content (***Table 1)***. Six oil mixtures of ethyl acetate and hexane were tested to simulate the diverse polarities found in commercial fragrances.

The hydrodynamic size and stability of the emulsions over 72 hours were evaluated by DLS. It was observed that mixtures containing more than 30% hexane (lower polarity index) became immiscible and could not dissolve polysorbate 80, leading to phase separation. Conversely, formulations with ethyl acetate:hexane ratios of 9:1 and 8:2 (Higher Polarity index) with a 1:2 surfactant-to-oil ratio consistently produced smaller and more stable droplets (~100 nm). Increasing the amount of oil increased the droplet size. The larger the droplet size, the greater the destabilisation of the emulsion in a shorter time. The main destabilisation mechanism identified was Ostwald ripening, especially in emulsions with more polar oils (***Figure 1)***. A reproducibility study was also performed, assessing droplet size across triplicate samples over 72 hours. Stability and reproducibility were retained in emulsions with surfactant-to-oil ratios of 1:2 and 1:3, particularly when the oil phase had a polarity index ≥0.232 (Ethyl acetate: Hexane 8:2 ratio or higher). Deviations in droplet size remained under 30 nm for stable formulations, confirming good reproducibility. Samples with high standard deviations or visibly altered appearance were deemed non-reproducible, particularly those with lower polarity indices or insufficient surfactant.

The influence of the aqueous phase was then studied. Since phosphate buffers are incompatible with calcium used in later gelation steps, alternative aqueous phases were explored. Emulsions prepared in water or HEPES buffer generally showed larger particle sizes and reduced stability. Adding NaCl at various concentrations (up to 0.16 M) increases the

emulsion stability [14], in the range of polarities studied, this effect was not observed. Increasing salts concentration in the aqueous phase did not significantly improve droplet size or stability, and in some cases, larger sizes were recorded after 24 hours, possibly due to solvent evaporation or increased polydispersity (***Figure 2)***. Although studied emulsions prepared in PBS showed superior properties, the use of MilliQ water was used for further encapsulation steps, as the emulsions could not interact with the alginate before gelification with thhe calcium ions to form the encapsulated system. Therefore, the use of water as a continuous phase was considered more appropriate for the final formulations.

Following the stability assessment of emulsions across different polarity systems (***Table 2)***, a versatile library of nanoemulsions was developed and subsequently encapsulated within a calcium-crosslinked alginate matrix. To ensure the applicability of this platform to diverse fragrance compositions, a sufficiently robust analytical method is now required to accurately determine encapsulation efficiency across various formulations.

To assess the encapsulation efficiency of microencapsulated systems, the GC-MS method was first optimized. The fragrance was analyzed at various temperatures (70°C, 90°C, 130°C, and 180°C) to determine the best conditions for signal detection. Higher temperatures revealed higher molecular weight and polarity compounds but also introduced noise and potential degradation of the encapsulation system. Therefore, 70°C was selected as the optimal analysis temperature, allowing detection of key volatile compounds while preserving signal clarity.

Three sample types were analyzed: the full reference fragrance, the non-encapsulated residual (free fraction), and the encapsulated sample. All were injected under identical headspace conditions. Controls, including blanks and empty capsules, confirmed no background interference (***Figure 3)***.

For a representative fragrance, a total of 18 representative peaks from the reference fragrance were selected for encapsulation efficiency calculations. For each signal, the area in the encapsulated sample was compared to the reference to quantify the percentage retained. Most compounds showed high encapsulation efficiencies between 70% and 97%. Two signals, however, exhibited significantly lower retention (around 50% and 0.24%, respectively), likely due to their volatility or limited interaction with the capsule matrix.The average encapsulation efficiency for the representative fragrance was calculated at 82.6%, based on the mean of the selected peak efficiencies. Signal variation between replicates remained low (<4%), confirming good reproducibility of the method.

3.1. Figures, Tables and Schemes

Table 1. *Different experiments performed to study the PIC method emulsion formation*

Aqueous phase	Oil phase	Surfactant:oil phase ratio (v:v)	% of aqueous phase
PBS 1X	Ethyl acetate	1:1 to 1:5	90
PBS 1X	Ethyl acetate: Hexane 9:1	1:1 to 1:5	90
PBS 1X	Ethyl acetate: Hexane 8:2	1:1 to 1:5	90
H_2O	Ethyl acetate	1:1 to 1:5	90

H_2O with different mM of NaCl	Ethyl acetate	1:1 to 1:5	90
HEPES	Ethyl acetate	1:1 to 1:5	90

Table 2. *Summary of key formulation factors influencing nanoemulsion formation via the PIC method*

Factor	Description	Effect on Emulsion
Addition Rate	Speed of adding aqueous phase to oil phase	Slower addition, smaller droplet size and higher stability
Oil phase polarity	Use of different ratios of Ethyl acetate: Hexane (v/v) Polarity index from 0.288 to 0.009	The best formulations from a polarity index of 0.232
Oil:Surfactant ratio	From 1:1 to 1:5	Best formulation at 1:2
Aqueous phase	PBS, HEPES solution, 0.016mM NaCl and water	No improvement is observed with increasing salinity. For this reason, water is used as the aqueous phase.

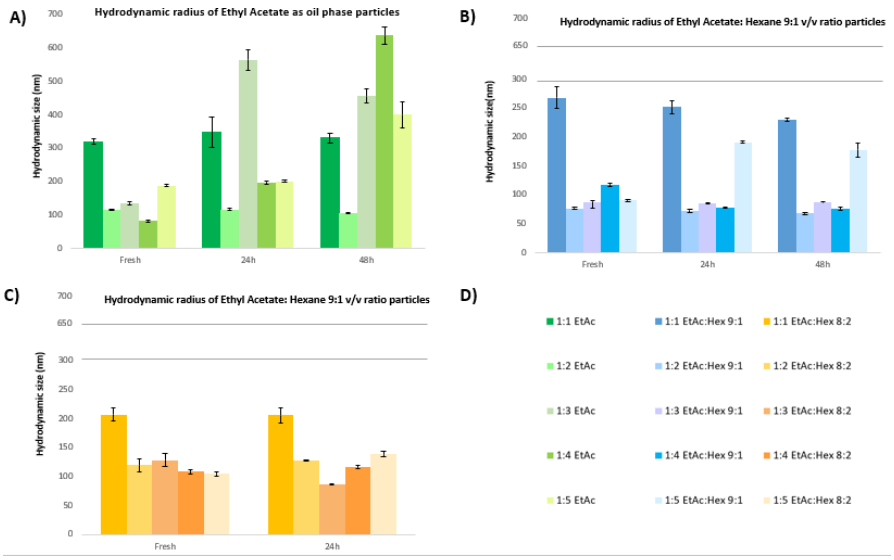

Figure 1. Hydrodynamic size of nanoparticles obtained from different oil phases, measured by DLS. A) Nanoparticles prepared with ethyl acetate (EtAc) as the oil phase at various surfactant-to-oil ratios, with standard deviations shown over 48 hours. B) Nanoparticles formulated with EtAc:Hexane (9:1 v/v) as the oil phase under the same conditions. C) Nanoparticles prepared using EtAc:Hexane (8:2 v/v) as the oil phase, characterized over 24 hours. D) Graph legend corresponding to panels A–C.

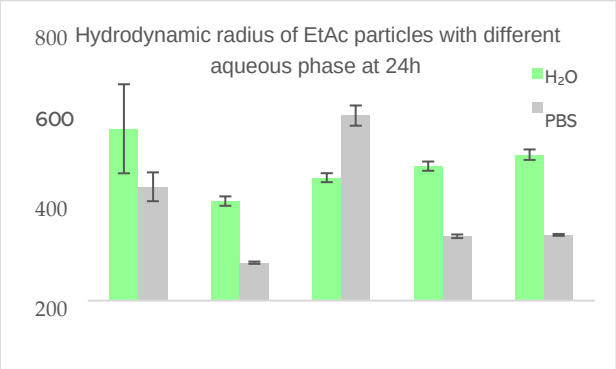

Figure 2. Characterisation of hydrodynamic size mean by DLS of different aqueous phase nanoparticles with their standard deviation at different surfactant: EtAc (v/v) ratios at 24 hours.

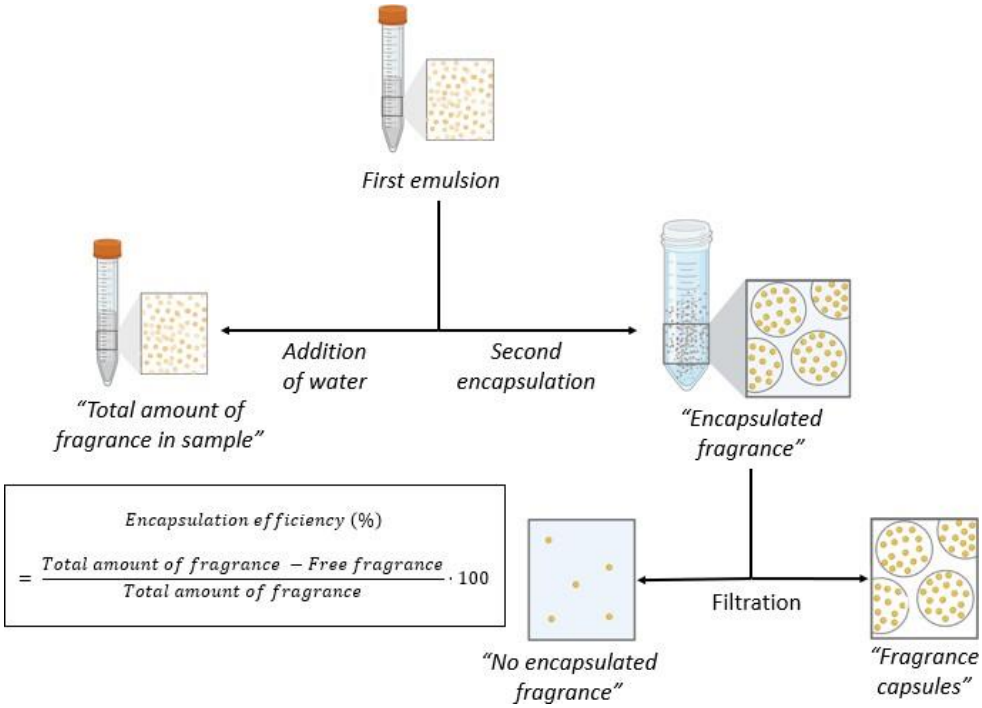

Figure 3. Scheme of the experimental procedure for determining the encapsulation efficiency of fragrance capsules. The fragrance encapsulation process begins with the preparation of the initial emulsion. The sample is then divided into two equal portions by weight. One portion, combined with an added volume of water, forms the total fragrance content of the sample. The second portion of the initial emulsion is used for a second round of encapsulation. The wastewater from the filtrate allows for the quantification of the unencapsulated fragrance.

4. Discussion

The process of NE formation using PIC proved to be suitable for highly volatile systems such as fragrances, providing stable emulsions with sizes compatible with subsequent encapsulation to form encapsulated microsystems. Nevertheless, studies revealed several critical insights into the behavior of nanoemulsions formed by the PIC method, especially concerning

oil polarity, surfactant concentration, and the aqueous phase environment. These findings laid a solid foundation for subsequent fragrance encapsulation efforts.

Firstly, the polarity of the oil phase plays a crucial role in emulsion stability. Mixtures with a higher ethyl acetate content (higher polarity index) favored more stable and homogeneous emulsions. The inclusion of a small proportion of a more hydrophobic solvent like hexane (as in the 9:1 and 8:2 ratios) appears to reduce Ostwald ripening, thereby improving stability. This supports the hypothesis that tuning oil polarity can mitigate inter-droplet migration and preserve droplet uniformity over time.

Then the optimal surfactant-to-oil ratio was found to be 1:2, which balanced droplet size and stability effectively. Ratios with too little surfactant failed to stabilize the interface, resulting in coalescence and polydispersity. Conversely, overly high surfactant content did not significantly improve stability and led to larger droplet sizes. Reproducibility data confirmed that stable emulsions could be reliably reproduced across batches, with size deviations remaining within acceptable margins. However, instability mechanisms such as flocculation and coalescence increased significantly when less favorable ratios or oil polarities were used, highlighting the importance of formulation optimization for consistent results.

The shift from PBS to alternative aqueous phases was necessary due to the incompatibility with calcium ions used in alginate gelation. Unfortunately, replacing PBS with HEPES buffer or adding NaCl did not fully restore the desirable emulsion properties. It is determined to use water as the aqueous phase, as the emulsion is sufficiently stable to allow the subsequent gelation of the alginate to obtain the encapsulated microsystem.

Once the emulsion was prepared and the fragrance encapsulated, it became essential to characterize the system and evaluate its encapsulation efficiency. The results obtained indicate that the microencapsulated system achieved an overall EE exceeding 80% for a representative fragrance, which is significant given the complex and variable composition of commercial fragrance mixtures.

However, the encapsulation behavior of individual compounds was not uniform. While most components were efficiently retained, certain molecules, particularly those with low volatility or greater affinity for the aqueous phase, were encapsulated less effectively. This highlights the significant influence of molecular properties such as weight, solubility, and polarity. The compound with the lowest EE (0.24%) likely exhibited limited incorporation into the oil phase or a strong preference for the surrounding aqueous medium, resulting in low retention.

The controlled addition of the aqueous phase proved to be a crucial factor. This fact reinforces the hypothesis that the stability of NE obtained by PIC depends not only on the phase proportions but also on the formation process. This observation coincides with previous studies that have shown that controlling the curvature transition of the surfactant improves the monodispersity and the stability of the generated emission.The study also shows that the use of water as a continuous phase is preferable to PBS, not only because of its compatibility with the calcium gelling process, but also because of the slight improvement in the measurement and stability of the NE. This choice contributes to a simpler and more economical formulation. Despite these variations, the GC-MS methodology proved robust and suitable for detecting and quantifying individual fragrance compounds. The decision to analyze samples at 70 °C was validated, allowing efficient volatilization without damaging the alginate matrix.This work opens the door to the future use of techniques such as SIR or MRM to improve selectivity and

reproducibility, especially useful in industrial environments. The system presents a good general performance, but it will be necessary to optimise it to improve the encapsulation of certain compounds and reduce the analytical variability, in order to ensure a more uniform and stable release in commercial applications.

Overall, these results demonstrate that the developed system is a realistic and functional alternative to the usual microplastics. The physicochemical characteristics, the effective fragrance delivery, and the sensory response show that it is possible to achieve similar or higher levels of efficiency with biodegradable materials such as alginate. Moreover, the simplicity of the process and the use of materials approved for cosmetic use facilitate industrial application. It will also be necessary to evaluate the effect of the final formulation on the skin and its integration with other cosmetic ingredients.

5. Conclusion

This study presents a sustainable encapsulation strategy for lipophilic fragrances based on sodium alginate microencapsulated system containing an internal oil-in-water nanoemulsion (O/W NE). The nanoemulsions were successfully formulated using Phase Inversion Composition (PIC), a low-energy method, which provided stable emulsions with controlled droplet size and narrow size distribution. A systematic study of emulsion stability and droplet size optimization was carried out to build a comprehensive library of nanoemulsions, serving as a foundation for understanding and designing suitable delivery systems for future fragrance encapsulation. The optimized oil-in-water nanoemulsion provided a stable platform with droplet sizes appropriate for retaining volatile compounds.

Non-spherical microcapsules were formed via internal gelation of sodium alginate using calcium ions. Encapsulation efficiency was evaluated using a headspace GC-MS method, comparing the volatile profile of encapsulated samples to maximum amount fragrance references. The method proved robust, especially when samples were analyzed at 70 °C, which ensured effective volatilization while preserving the structural integrity of the alginate capsules. Results showed a high overall EE (>80%) for a representative fragrance, although variability among individual compounds was observed. Compounds with lower volatility or higher aqueous affinity were less efficiently retained, highlighting the importance of physicochemical compatibility between fragrance components and the encapsulation matrix.

Overall, this biopolymer-based encapsulation platform offers a promising alternative to conventional systems that rely on non-biodegradable materials. It combines effective fragrance retention, controlled release, and environmental safety. While further optimization is still possible, the proposed system aligns well with current trends in green chemistry and regulatory demands for microplastic-free cosmetic formulations.