CHITOSAN-BASED MICROCAPSULES FOR ESSENTIAL OIL VIA IONIC GELATION

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TÓM TẮT

TỔNG HỢP HẠT MICROCAPSULE CHỨA TINH DẦU TỪ POLYMER SINH HỌC CHITOSAN BẰNG PHƯƠNG PHÁP ION HÓA TẠO GEL

Nghiên cứu tập trung tổng hợp polymer sinh học Chitosan (CS) có nguồn gốc từ Chitin và các hạt Microcapsule Chitosan bọc tinh dầu sả chanh(CSO) được điều chế bằng phương pháp gel ion để tạo liên kết ion giữa CS với Sodium Tripolyphosphate (STPP). Các đặc trưng của hạt CS, CS – STPP, CSO được xác định bằng kính hiển vi điện tử quét (SEM), kính hiển vi quang học (OM) và đánh giá phân bố kích thước hạt bằng tán xạ ánh sáng động (DLS). Ảnh hưởng của các thông số pH và thời gian phản ứng giữa CS và STPP cũng như vai trò của STPP đến quá trình hình thành hạt Microcapsule CSO đã được nghiên cứu. Kết quả chỉ ra hạt Microcapsule có khả năng bao bọc lấy tinh dầu bên trong khi STPP tạo liên kết ngang với CS bằng liên kết ion. Kích thước hạt CSO phân bố nhiều nhất từ 40 – 80 μm. Thông số thực nghiệm để tạo CS-STPP tối ưu là nồng độ STPP 1% ở môi trường pH 9 và thời gian phản ứng tối ưu là 2h.

Từ khóa: *Microcapsule, Chitosan, tinh dầu, Ionic gelation, STPP, morphology, encapsulation*

1. Introduction

In Vietnam, the shrimp farming industry is rapidly expanding. Along with this growth is a significant increase in by-products such as shrimp heads and shells. These by-products contain many of organic substances, soluble proteins, and carbohydrates. However, if not adequately treated, they can cause severe environmental pollution. Many studies have been conducted to convert these by-products into chitin/chitosan (CT/CS) to address this issue. Chitosan (CS) is known as an excellent biopolymer with great potential for applications in various fields, such as functional additives for medicine, pharmaceuticals, agriculture, and cosmetics [1].

The use of CS-based microcapsule technology enhances cosmetic formulations by improving stability and protecting active ingredients from environmental degradation. Depending on the nature of interactions between materials, various encapsulation methods—such as chemical, physicochemical, and mechanical techniques—can be employed. To enhance the applicability of CS, research groups have modified it into different forms to suit specific applications. In agriculture, CS microcapsules enable the controlled release of agents such as pesticides and herbicides, supporting organic farming practices [2]. Doan et al. fabricated curcumin-loaded CS nanocapsules using the coaxial electrospraying method [3]. Additionally, other studies have developed antibacterial polymer films based on lemongrass essential oil and CS using the solution

casting method [4]. However, research on chitosan modification, especially with chelating agent for encapsulating essential oil application remains limited in Vietnam.

The study focused on synthesizing the biopolymer chitosan derived from chitin and preparing chitosan-based microcapsules encapsulating essential oils (CSO) using the ionic gelation method to form ionic bonds with sodium tripolyphosphate (STPP). The characteristics of the resulting CS-STPP microcapsules and CSO were evaluated using scanning electron microscopy (SEM), Optical Microscopy (OM) and particle size distribution was evaluated using dynamic light scattering (DLS). pH and reaction time parameters were investigated, and the results showed that chitosan successfully bonded with STPP, reducing particle size, with optimal experimental conditions being 1% STPP concentration at pH 9.0 and a reaction time of 2h. The investigation into particle morphology and size distribution under varying parameters provides a solid foundation for structural optimization. The findings based on the synthesis of chitosan microcapsules encapsulating essential oils offer valuable insights for advancing the practical utilization of natural polymers for the encapsulation of essential oils, with eco-friendly technologies.

2. Materials and methods

2.1. Materials

Chitin derived from shrimp shells, practical grade, coarse flakes was purchased from Sigma-Aldrich. Lemongrass citral 80 essential oils with two main isomeric aldehydes (approximately 80%), namely isomers geranial (α-citral) and neral (β-citral), was supplied by Aota company (Vietnam). Double distilled water was used throughout the study. Otherschemicals used (sodium hydroxide, acetic acid, sodium acetate, sodium tripolyphosphate (STPP, $Na_5P_3O_{10}$) were purchased from China without further purification.

2.2. Synthesis of Chitosan

In a typical experiment, a CT solution (prepared by dissolving CT in NaOH 50%) was first stirred at 70 ^oC in 1h. Then, the mixture was rinsed with ethanol 70% and water until pH 7.0. The CS solid was obtained by drying on the plate at 60 ^oC. The concentration of NaOH influences the subsequent dissolution of the formed chitosan-tripolyphosphate (CT) complexes in 1% acetic acid.

2.3. Synthesis of Microcapsule CS/ STPP

In this process, STPP was first dissolved in water and various pH solution between 3 and 9 was investigated. Separately, CS was dissolved in a 1% acetic acid solution, achieving a solubility of 99,23%. The remaining undissolved CT was weighed at 0,0023g. The chitosan solution was then added dropwise to the STPP solution and the mixture was stirred at 120 rpm for 1 to 3 hours at room temperature, to stabilize the particle structure. The resulting microcapsules were soaked for 24 hours to stabilize them. Finally, the resultant products were filtered, washed, and dried at 50°C for 2 hours to obtain solid CS/STPP microcapsules.

2.4. Synthesis of Microcapsule CSO

The synthesis procedure of chitosan-based microcapsules encapsulating lemongrass essential oil (CSO) with STPP using the ionic gelation method or without STPP was displayed in Figure 1. CS was first dissolved in acetic acid, followed by an injection drop of lemongrass essential oil

dissolved in methanol. The resulting mixture (Solution A) was then dropwise added to an STPP solution previously prepared to induce ionic crosslinking. Without STPP, the solution A was stabilized for 24 hours at room temperature, followed by filtration and thorough washing with water. Finally, the microcapsules were dried at 50°C for 2 hours to obtain solid CSO microcapsules.

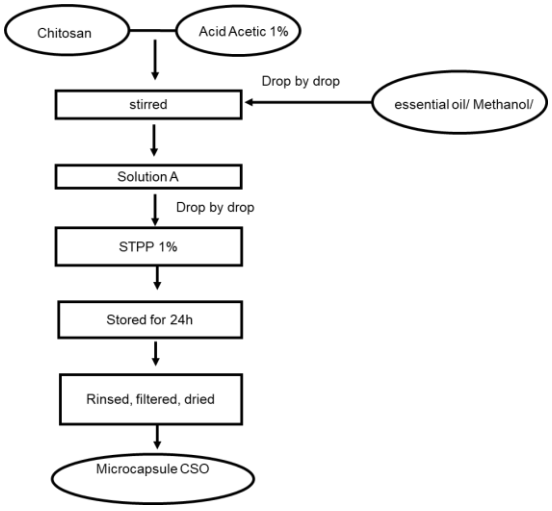

Figure 1. *Schematic of preparation process of CSO microcapsules*

2.5. Characterization of obtained CS and CS/STPP microcapsules.

CT and CS were characterized by Scanning Electron Microscopy (SEM), the CS/STPP and CSO microcapsules were analyzed via Dynamic Light Scattering (DLS) and Optical Microscopy (OM) with various magnification (50,100,200,500). The SEM analysis was processed using Quanta 250 at 10 kV. Before the imaging, samples were fabricated on Carbon stubs and coated with a thin film of Pt–Au under 5 mA sputtering to make them conductive (Thermo Fisher Scientific Co., US).

2.5. Data Analysis

The experiments were conducted in triplicate in the similar condition to ensure the reliability of the statistical analysis. The data processing was performed using Microsoft Excel.

3. Results and Discussion

3.1. Characterization of Chitosan

SEM images shown in Figure 2 reveal that synthesized CS has a smoother and more uniform surface than CT. CS demonstrates superior chemical and biological interaction, along with good moisture absorption. However, the surface morphology and properties of CS can vary depending on the original CT source. These observations were also reported in previous research [5].

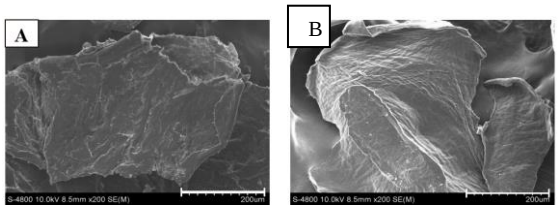

Figure 2. *SEM images of Chitin (A) and Chitosan (B).*

3.2. Effect of pH of STPP solution on the formation of CS Microcapsule

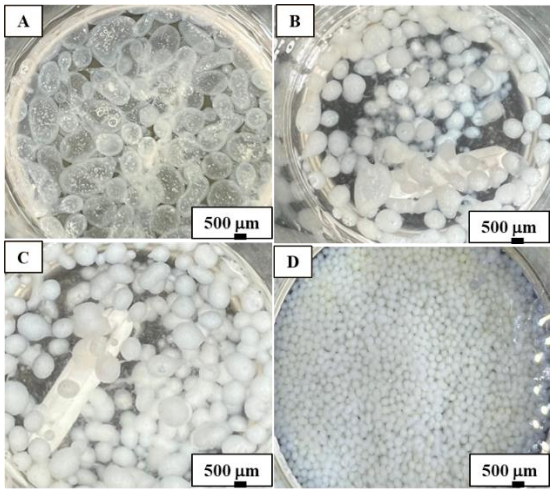

Figure 3*. Effect of pH on the morphology of CS/STPP Microcapsule at various pH : A) pH 3; B) pH 5; C) pH 7; D) pH 9.*

The morphology of CS/STPP microcapsules varies depending on the pH condition during synthesis (Figure 3).

Chitosan becomes protonated in acidic environments, forming ion -pair complexes with STPP as presented in Figure 4. STPP releases phosphate ions (PO_4^{3-}) in water, and its pH influences the cross-linking behavior with CS [6, 7]. At low pH, cross-linking is less efficient due to low molecular packing, resulting in uneven and transparent microcapsules, although the size is quite large, as shown in Figure 3.

As the pH increases, the microcapsules become more opaque, stable, and uniform in shape and size. At pH levels of 5 and 7, the resulting particles are relatively large and display significant size heterogeneity. At pH 9, microcapsules form with high uniformity with denser shell structures and smaller sizes and enhanced stability. This is due to the combined interaction of OH^- and PO_4^{3-} ions with NH_3^+ groups and the increased flexibility of CS chains, leading to stable and thermally resistant microcapsules (Figure 4) [8, 9].

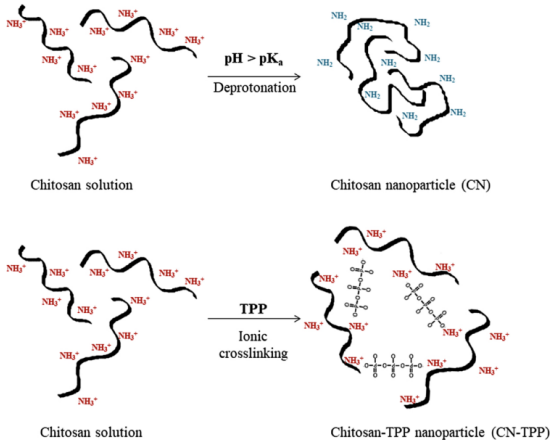

Figure 4*. Mechanism of protonation of amine group I of CS and ionic cross-linking between CS and TPP [9]*

3.3. Effect of reaction time on CS Microcapsule granulation

Reaction time is a critical factor affecting the characteristics of CS/STPP microcapsules. At 15 minutes, the microcapsule shells appear pale white and uniform in size but are relatively large due to the initial cross-linking and water retention in the polymer network. The structure at this stage consists of a loose framework formed by early-stage bonding between CS and STPP [10].

When the reaction time increases to 60 minutes, the shells become more opaque, and excess water begins to escape, reducing the particle size. Some capsules, however, still retain a pale white appearance. Cross-linking intensifies at 2–3 hours, resulting in fully opaque shells with uniform color and morphology. STPP is completely cross-linked with CS at this stage. Overall, extended reaction time leads to smaller, denser and more uniformly white microcapsules, indicating a higher cross-linking density [11]. The optimum reaction time of 2h was selected for the subsequent investigation.

3.4. Synthesis of Microcapsule CSO

The morphology and particle size distribution of chitosan (CSO) microcapsules, were investigated using optical microscopy and analyzed via dynamic light scattering (DLS) (Figure 5).

In the absence of STPP, the microcapsules displayed a relatively uniform size distribution, with diameters predominantly ranging from 2 to 10 µm. Upon incorporation of STPP, a significant increase in particle size was observed, with most particles falling within the 40–80 µm range. Additionally, a core–shell structural morphology became apparent, and the particle size distribution was notably more heterogeneous.

This variation is attributed to the aggregation of oil droplets prior to encapsulation and the ionic crosslinking between STPP and chitosan. As previously discussed, STPP dissociates

into PO_4^{3-} and OH^- ions, which interact electrostatically with the protonated amine groups (NH_3^+) of chitosan, promoting network formation and leading to larger particle sizes.

The increase in microcapsule size aligns with the objective of modulating the release profile of the encapsulated essential oil. Smaller microcapsules tend to release their contents more rapidly, resulting in reduced stability under environmental factors such as light, temperature, and humidity. In contrast, larger microcapsules provide enhanced structural integrity and enable a more sustained release under varying environmental conditions [9].

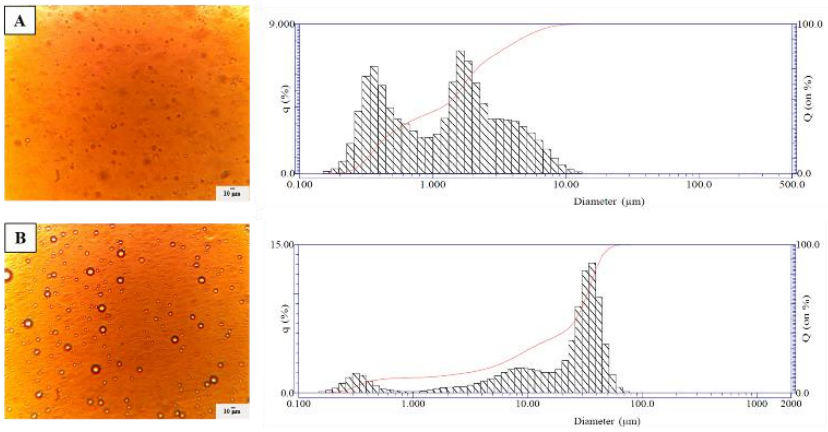

***Figure 5**. The morphology and particle size distribution of CSO (A) without STPP and (B) with STPP*

4. Conclusion

This study successfully demonstrated the synthesis of chitosan from shrimp shell-derived chitin, achieving a high solubility of 99.23% in 1% acetic acid under optimized conditions (50% NaOH, 70 °C, 1 hour).

This study presents preliminary results on the synthesis of chitosan-based microcapsules encapsulating essential oils using STPP as a crosslinking agent. The microcapsules were effectively fabricated via ionic crosslinking with sodium tripolyphosphate (STPP), with optimal encapsulation conditions determined to be 1% STPP, pH 9, and a reaction time of 2 hours. The incorporation of STPP significantly influenced the morphology and size distribution of the microcapsules, contributing to enhanced structural stability and potential for controlled release.

In future work, we aim to optimize the encapsulation conditions, including STPP concentration, reaction time, and essential oil loading efficiency. Further characterization will be conducted to assess physicochemical properties, encapsulation efficiency, and release kinetics. These investigations will contribute to a deeper understanding of the material system and its potential applications in fields such as food preservation, pharmaceuticals, and cosmetics.

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