

Evaluation of the colloidal/chemical performance of core-shell nanoparticle formed by zein and gum Arabic

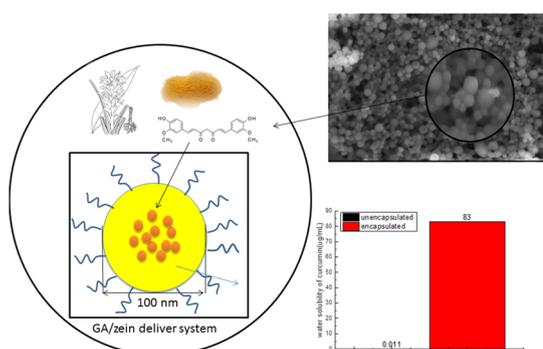


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GRAPHICAL ABSTRACT



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ABSTRACT

To evaluate the performance of biopolymer fabricated nanoparticle under commercial processing conditions, the stability of gum Arabic (GA)-zein-cur (curcumin) colloidal system was recorded and analyzed. The results showed that GA-zein-cur system is colloidal stable in the pH range of 5–8, however, encapsulated curcumin degraded rapidly as long as the pH changes. As for processing temperature, more than 70 °C will affect the spatial structure of zein and leading to the leak or exposure of encapsulated curcumin which result in the degradation of curcumin. Na⁺ has no significant effect on colloidal and chemical performance of nanoparticles while Fe³⁺ could penetrate the zein nanosphere and compromise curcumin. Results of our work imply that the protein-based core-shell delivery system has advantages in solubilizing the hydrophobic compounds and has certain ability to protect the encapsulated material against the unfavorable environment.

1. Introduction

Encapsulation has been an increasingly developed technique to solubilize and protect even targeted-deliver the sensitive compounds such as curcumin, β-carotene and lutein [1–4]. These compounds are edible and potentially health-promoting, for example, curcumin is anti-oxidant, anti-microbial, anti-inflammation, hypolipidemic and even

anti-carcinogenesis [5–7]. Health-promoting effects are mainly contributed by the chemical structures of the sensitive compounds such as functional groups and alkyl chains. However, chemical structures are also responsible for the sensitivity and low solubility/bioavailability of the compound [8]. Encapsulation is one of the most convenient ways to increase the solubility and protect the sensitive compound including drugs and nutrients while could also contribute to targeted-delivery

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[9–11].

Encapsulation with biopolymers has advantages such as safe and compatible in the human body and therefore been widely applied. Usually, biopolymer fabricated nanoparticles consist of core and shell, the core forms a nanosphere with hydrophobic interior and hydrophilic exterior, the shell is mostly polysaccharide could provide enough repulsion force between the nanoparticles [12]. Proteins (Zein, casein, β -lactoglobulin) [13–16], modified starch (cyclodextrin) [2] and polysaccharides (chitosan, pectin) [17,18] has been reported to serve as a core material. Among these materials, zein is the most reported material which is an amphiphilic protein extracted from corn, property of self-assembly has made it the most popular core material for drug/food delivery [13,19–21].

Actually, zein has been widely used as delivery vehicles for hydrophobic active molecules [13,20,22,23]. However, protein is sensitive to the environment, secondary and tertiary structure is affected by the environmental conditions such as ionic strength, pH, temperature [24,25]. Previous studies have mostly focused on improving solubility, bioavailability of active substances and the colloidal stability of nanoparticles [3,26–29]. But nonetheless stability of the encapsulated material requires stability assessments too.

Our previous work has identified that the encapsulation efficiency of GA-zein is 95.9% and the solubility of curcumin is about 11 ng/mL while the GA-zein delivery system improves its solubility to 83 μ g/mL, about 7200 times enhancements [30]. Hence, this study investigated the protective effect of GA-zein to the curcumin and stability of GA-zein-cur system under different environmental conditions. Results of this study could be directly applied in food coloring design but also could contribute to the controlled release of the curcumin.

2. Materials and methods

2.1. Materials

Curcumin (> 98%) was purchased from Henan Zhongda Biology Ltd Co.; Zein was obtained from TCI (Tokyo Chemical Industry) (shanghai) Development Ltd Co.; Gum Arabic was bought from Aladin (shanghai); other chemicals, such as sodium hydroxide, anhydrous ethanol, ferric trichloride and hydrochloric acid were all analytical grade and used without further purification.

2.2. Preparation of nanoparticles

2.2.1. Solution preparation

Zein (200 mg) and curcumin (20 mg) were dissolved into ethanol aqueous solution (ethanol: deionized water = 80:20 v/v) with magnetic stirring at room temperature for 1 h (seal the beaker in case of evaporation). 300 mg GA was added into 250 mL deionized water and stirring for 5 h as the anti-solvent. After full dissolution of the anti-solvent, it was rapidly transferred into zein-curcumin solutions. Resulting solution was evaporated with a rotary evaporator at 35 °C to eliminate the organic solvent. Organic evaporated dispersion was collected and diluted ten times before tests.

2.2.2. Powder preparation

Same solution preparation method as 2.2.1 and vacuum freeze drier (FD-1C-50, Boyikang, China) was hired to lyophilize the GA-zein-cur dispersion.

2.3. Morphology observation

Zein and curcumin were dissolved as 2.2.1 and evaporation with rotary evaporator, followed by freeze drying. The lyophilized powder was evenly and gently placed on the stainless steel base and the base was transferred into the sample chamber. SEM experiments were conducted with SUPRATM5 (Carl Zeiss AG, Germany), acceleration voltage

is in the range of 0.02–30 kV. Images were taken with a nominal magnification 20,000 \times .

2.4. Stability analysis

There are two facets to the stability of the GA-zein-cur nanoparticles. First is the chemical stability of the encapsulated curcumin. Chemical structural changes of curcumin will weaken the coloring performance as well as the biological functions. Second point is whether the colloidal system is stable enough to exclude precipitation.

2.4.1. Chemical stability of curcumin

2.4.1.1. Chromatic aberration measurements. Portable ChomaMeter (CR-400, Bruke, Germany) was employed to determine the L^* , a^* and b^* value of the GA-zein-cur. L^* , a^* and b^* values were measured through a quartz colorimetric utensil and the reference material is a white tile ($L^* = 97.43$, $a^* = 0.01$, $b^* = 1.64$). Total color difference (ΔE^*) can be calculated by the Eq. (2). Curcumin degradation kinetics Eq. (3), preservative rate (1) and half-life period (4) could be calculated by the equations.

$$\text{preservative rate} = b_t^*/b_0^* \quad (1)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (2)$$

$$\ln(b_t^*/b_0^*) = kt \quad (3)$$

$$t_{1/2} = \ln 2/K \quad (4)$$

2.4.2. Stability analysis of the colloidal system

2.4.2.1. Particle size measurements. Diameters of nanoparticles were measured by dynamic light scattering (Nano-ZS, Malvern instruments, UK). Mean diameters were calculated by surficial area weighted average $D_{3,2}$ and volumetric weighted average $D_{4,3}$. Refractive index of the zein protein was set as 1.590 while the refractive index of aqueous phase was 1.330. All samples were diluted to avoid multiple scattering effects before tests.

2.4.2.2. Particle charge measurements. A micro-electrophoresis device (Nano-ZS, Malvern instruments, UK) can be used to examine the particle charges. Samples were diluted before tested.

2.5. Stability on environmental stress

Chemical/colloidal stability of GA-zein-Cur will be influenced by many environmental factors, it's necessary to evaluate the chemical/colloidal stabilities under certain conditions. All measurements were performed after the samples were exposed to simulated condition for enough time.

2.5.1. Effect of sunlight exposure

Curcumin powder was dissolved in 80% ethanol-water solution (v/v) and the absorbance value of curcumin under 425 nm was set as 1. Expose curcumin and diluted GA-zein-cur dispersion under sunlight, take samples every certain time and measure the color changes, mean diameters and zeta potentials.

2.5.2. Effect of processing pH

Diluted GA-zein-cur was dispensed into 6 brown bottles and pHs were adjusted by certain concentration of NaOH or HCl solution to 3, 4, 5, 6, 7, 8, respectively. Store the dispersion under room temperature, data collected including zeta potentials, mean diameters and b^* values to decide the degradation kinetic equation as well as half-life.

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