Post-Harvest Application of Tara Gum Coating Incorporated With Silver Nanoparticles for Preservation of Banana

Jhonatan Rafael de Oliveira Bianchi, Saymon Menezes de Souza, Igor José Boggione Santos

1 Federal University of São João del Rei (UFSJ), Alto Paraopeba Campus. Chemistry. Biotechnology and Bioprocess Engineering Department (DQBIO). Ouro Branco. Minas Gerais. Brazil

* Correspondence: igorboggione@ufsj.edu.br (I.J.B.S);

Abstract: The use of natural nanocomposite to increase shelf-life has gained space in the packaging sector. Therefore, this research produced a Tara Gum coating with Silver Nanoparticles (AgNP) for banana cv. Caturra conservation. The AgNP synthesis was optimized by an experimental design, the size as a dependent variable. The best points were: 300 rpm of stirring, the temperature of 25 ºC, and the reagent flow of 2.5 mL·min⁻¹. The obtained size was 20.08 ± 0.17 nm, and Polydispersity Index was 0.321 ± 0.047 nm. Transmission Electron Microscopy showed smaller particles than 100 nm and dispersed. The rheological study presented the Tara Gum solution as a pseudoplastic fluid, and the addition of AgNP did not alter Tara Gum's rheological behavior. The coating could slow up the fruit skin ripening; withholding in 2 % the weight loss; increasing the resistance; increasing 88 % of malic acid content, while the control sample increased just 24 %; and kept °Brix in low levels.

Keywords: nanocomposite; galactomannan; rheology.

© 2022 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

The industrial food chain has huge importance and impact on all the world. Fruits and vegetables are the most utilized commodities, often consumed in natura. Also, fruit and vegetable processing can export these commodities [1]. However, there are two main problems in the food chain: i) the loss of nutrients and important compounds for human health and ii) the waste and losses. To solve the first one is the possibility to commercialize fresh fruits. This could amplify the losses during transportation because of the fruits and vegetable perishability. One solution to minimize the losses is packaging that can extend the fruit shelf-life [1,2].

Biopolymer matrix-based nanocomposites have got the attention in the recent literature once it is biodegradable and biocompatible. These materials have higher strength, workability and flexibility, great barrier properties, heat resistance, and lower flammability, among other properties[3]. Using these materials in packaging is a great alternative to increase food quality and safety and extend shelf-life, expanding the market and reducing food problems such as waste and loss. It happens because the nano-biopolymer will protect food from oxidative changes, spoilage, and the growth of microorganisms [3,4]. These had created a new era for edible coating, mainly with the advent of nanotechnology.
The development of new coating based on natural or synthetic polymers combined with other nanostructures can control fruit maturation by the environment, gas mass transfer controlling, and exhibit antimicrobial activity [5]. Metallic nanoparticles, mainly Silver Nanoparticles, has been used because of their antimicrobial property; they can react with the thiol group of cells of microorganisms and inactivate or kill it [6]. The toxicity of nanoparticles depends on the size, shape, solubility, stability, and chemical structure. Among all metallic molecules, Silver Nanoparticles (AgNP) have less toxicity in animal cells [7]. Once it is a stable colloid and can be considered safe and non-toxic, it can be used in food packaging combined with biopolymers [8].

There are several examples of natural gum as a coating for fruit preservation. The most common is chitosan, carboxymethyl celluloses, Arabic gum, xanthan gum, guar gum, and other plant-based starch; these biopolymers are sustainable and substitute for petroleum-based polymers [9]. These materials were able to extend the shelf-life of apple, banana, orange, tomato, mango, e other fruits [4,5,10,11]. A chitosan-aloe vera gel could delay mango maturation reduce weight loss, respiration rate, and ethylene production. Therefore this coating suppressed diseased maintained natural proprieties of mango fruit [12]. Another study demonstrated that rice starch coating blended with sucrose esters could delay banana maturation [13]. Due to all of it, is poured in the literature the use of Tara Gum as biopolymer coating.

Tara Gum is a non-toxic biopolymer extracted from seeds of the Caesalpinia Spinosa tree can be used in food industries as a thickener and stabilizer. Tara Gum is a network of polysaccharides composed of a linear chain of (1-4)-β-D-manopiranosil and lateral chain of (1-6)-α-D-galactopiranosil [13]. The polymer also has high hydrophilicity, and added with a uniform dispersion of nanoparticles can lead to a higher interfacial area, reinforcing its characteristics [15]. The gelation proprieties and the rheological characteristics are important for coating application and industrial use. Also, biodegradability and biocompatibility made Tara gum a potential biopolymer with much commercial interest [15].

Therefore, the nano-based biopolymer, or nanocomposite, can cause a huge social and economic impact in agribusiness, reducing the biggest world's problems: wastage, and consequently, increasing the food quantity available and reducing the famine [16].

Due to that, we present the use of the design of experiments to optimize the silver nanoparticle wet synthesis. So we incorporate these AgNPs in the tara gum solution applying in Banana Caturra to observe the effects on fruit maturation. Therefore, this work aimed to analyze the efficiency of a Tara Gum packaging with Silver Nanoparticles applied in bananas to extend its shelf-life. It is expected to present a new sustainable technology that meets the technological demands in the global fruit market.

2. Materials and Methods

2.1. Silver nanoparticles synthesis.

The synthesis methodology of silver nanoparticles followed the methodology described and adapted by Raza et al. (2016) [17]. With controlled flow, sodium citrate 1 mmol·L⁻¹ solution was dripped in silver nitrate 1 mmol·L⁻¹ solution under stirring. Immediately after the dripping, a sodium borohydride 4 mmol·L⁻¹ solution was added in the ratio 1:1:4, respectively. The dispersion stays stirring for another minute.
The Central Rotational Compound Design (CRCD) was performed with three replicates at the central point to predict the factor influences in response. The factor is the temperature (30 and 70 °C), drip flow (1.5 and 2.5 mL·min⁻¹), and stirring (150 and 250 rpm). Seventeen assays were performed, and combinations levels are described in Table 1 in coded and uncoded values of the experimental matrix. The response surface methodology was used to find out the significant factor and the optimal conditions for AgNPs synthesis [18,19].

Table 1. Combination and values of the experimental matrix with the mean of the obtained nanostructure hydrodynamic radius and the respective PDI.

| Assay | Flow (mL·min⁻¹) | Temperature (°C) | Stirring (rpm) | Hydrodynamics radius (nm) | PDI       |
|-------|-----------------|-----------------|----------------|---------------------------|-----------|
| 1     | 1.5 (-1)        | 30 (-1)         | 150 (-1)       | 91.58 ± 0.42              | 0.231 ± 0.031 |
| 2     | 1.5 (-1)        | 70 (1)          | 250 (1)        | 19.38 ± 2.55              | 0.280 ± 0.028 |
| 3     | 2.5 (1)         | 30 (-1)         | 250 (1)        | 20.08 ± 0.17              | 0.321 ± 0.047 |
| 4     | 2.5 (1)         | 70 (1)          | 150 (-1)       | 89.61 ± 7.75              | 0.237 ± 0.000 |
| 5     | 2.0 (0)         | 50 (0)          | 200 (0)        | 14.08 ± 7.26              | 0.351 ± 0.058 |
| 6     | 1.5 (-1)        | 30 (-1)         | 250 (1)        | 14.30 ± 1.65              | 0.365 ± 0.013 |
| 7     | 1.5 (-1)        | 70 (1)          | 150 (-1)       | 70.48 ± 11.32             | 0.584 ± 0.002 |
| 8     | 2.5 (1)         | 30 (-1)         | 150 (-1)       | 60.71 ± 4.46              | 0.512 ± 0.007 |
| 9     | 2.5 (1)         | 70 (1)          | 250 (1)        | 130.43 ± 37.67            | 0.453 ± 0.007 |
| 10    | 2.0 (0)         | 50 (0)          | 200 (0)        | 73.15 ± 10.23             | 0.545 ± 0.059 |
| 11    | 1.2 (-α)        | 50 (0)          | 200 (0)        | 98.44 ± 7.46              | 0.539 ± 0.037 |
| 12    | 2.8 (α)         | 50 (0)          | 200 (0)        | 15.15 ± 0.28              | 0.586 ± 0.038 |
| 13    | 2.0 (0)         | 16 (-α)         | 200 (0)        | 18.28 ± 0.54              | 0.536 ± 0.038 |
| 14    | 2.0 (0)         | 84 (α)          | 200 (0)        | 17.94 ± 2.69              | 0.442 ± 0.024 |
| 15    | 2.0 (0)         | 50 (0)          | 116 (-α)       | 155.55 ± 1.91             | 0.333 ± 0.011 |
| 16    | 2.0 (0)         | 50 (0)          | 284 (α)        | 157.60 ± 4.67             | 0.259 ± 0.001 |
| 17    | 2.0 (0)         | 50 (0)          | 200 (0)        | 33.17 ± 3.70              | 0.635 ± 0.039 |

2.2. Characterization of the nanostructure.

The NanoZeta sizer (Malvern, England) was used to determine the hydrodynamic radius (HR), the polydispersity index (PDI), and Zeta Potential (ζ). The measurements were performed without purification after obtaining the nanostructure using an avalanche photodiode detector (Brookhaven BI-APD, USA) and a correlator (TURBOCORR, Brookhaven, USA). The light source (CVI Melles Griot, USA) was a HeNe laser of 35 mW of power and λ = 632.8 nm, linearly polarized. For intensity control, and across polarizer system was used. The scattered intensity was measured under a fixed detection angle of 173° relative to the incident beam, and the CONTIN algorithm analyzed intensity autocorrelation functions for determining the size distribution.

Transmission electron microscopy (TEM) images were obtained at the National Nanotechnology Laboratory (LNNano) at CNPEM-Brazil. The microscope was a TEM JEOL-1400 PLUS (120 kV), with lanthanum hexaboride filament (LaB6) and equipped with a Gatan OneView camera 4Kx4K pixel. Before fixing the sample to the copper grids, they were discharged electrically by the Pelco easiGlow-Ted Pella (USA) discharge system at 15 mE for 10 s to improve their wettability. Subsequently, a drop of the suspension of nanostructure was added to the 400-mesh copper grid with carbon type B. After 30 s, the excess sample was removed with filter paper. The grid remained at room temperature until dry and was stored for further analysis via TEM. These images were used to obtain the size values of the nanoparticles using the software ImageJ 152a.
2.3. Tara Gum and AgNP nanocomposite.

A Tara Gum (GastronomyLab) solution of 1.5 % (w/v) was prepared for the coating in distilled water at room temperature. The Tara Gum (TG) was gradually dissolved under stirring at 25 ºC. After complete dissolution, silver nanoparticles were added in concentrations of 1, 3, and 5 % (v/v), according to the FDA (Food and Drug Administration) list of food additives, ranging from 1 to 10 %.

2.3. Nanocomposite realogy.

The rheological study of the nanocomposite was carried out on the Brookfield Viscometer equipped with a cylindrical probe. The rotation varied from 0 to 50 s\(^{-1}\), measured up and down curves. The experiments were carried out at 30 ºC. The effect of the temperature on the viscosity was analyzed between the temperatures of 20 to 80 ºC at 10 ºC intervals in the rotation of 10 s\(^{-1}\).

2.4. Tara Gum coating application in Caturra Banana.

Bananas were harvested in the first stage of maturation (totally green) by a rural producer and transported to the laboratory after 2 days. These were previously sanitized in a water tank and neutral detergent for 5 min to clot the latex. After washing with water, the fruits were selected and immersed in a 0.5 % (v/v) sodium hypochlorite solution for 3 min.

The fruits were divided into 8 groups for analysis over 14 days with 2-day intervals. Bananas were divided into 5 subgroups in each group, with 3 bananas each. The bananas were not treated; in the TG subgroup, the fruits were treated only with the gum solution. In the TG + 1 % (w/v), TG + 3 % (w/v), and TG + 5 % (w/v) subgroups, bananas were treated with gum solution with AgNP 1, 3, and 5 % (w/v), respectively. The 1, 3 and 5% (w/v) silver nanoparticle dispersions have silver content of 0.0004, 0.0012 and 0.002% (w/v). The temperature of storage was 25 ºC simulating the consumer storage conditions.

The effects and efficiency of the Tara Gum nanocomposite in the treatment of post-harvest bananas were carried out through non-destructive analyzes (weight loss and color changes) and destructive analyzes (firmness, pH, titratable acidity, and soluble solids).

The color change of the banana, due to the ripening, was analyzed by chromameter space LAB, through programs such as Photoshop [20]. Pictures were taken in the same environmental light intensity using a mobile (iPhone 6 – model A1586, Apple). \(L, *a, \) and \(*b\) values were collected in five distinct points. The hue angle was calculated by Equation 1., where 120º represents the green color, and 90º represents a yellow color.

\[ H^\circ = \tan^{-1} b^* / a^* \]  

The weight was got on an analytic scale before coating application and in each period of evaluation. The result is shown as a percentage of the difference according to Equation 2.

\[ WL = 100 - (W_{final} \times 100) / W_{initial} \]  

A conical probe evaluated the firmness through a digital penetrometer (DD-2000 Instrutherm) in four equidistant points. The strength detected in Newtons is directly proportional to the coating efficiency, showing the fruit resistance or not to the ripening.

The fruit was processed (10 g) (Mixer inox, Mondial) with 50 mL of distilled water and filtered in a conventional filter. The pH value was evaluated, from the filter, by pH meter (stand digital pH meter DM-22, Digimed). The Titrated Acidity (TA) was evaluated in malic acid.
percentage from the same filters Equation 3 [21]. 5 mL of the filtered were titrated with NaOH 0.1 mol·L\(^{-1}\) until the color turning point (with phenolphthalein).

\[
AT = \frac{(V_x M x f x 100)}{w}
\]

\(V = \) volume of sodium hydroxide used to titrate in mL.
\(f = \) malic acid correction factor: 0.067[21].
\(w = \) extract weight in grams.
\(M = \) sodium hydroxide solution molarity.

Soluble solids content (SS) was evaluated with the reading of 10 g of processed samples and diluted with 50 mL of distilled water in a portable Refractometer (RTA-50, Instrutherm). Results were expressed in °Brix (g of soluble solids/100 g of sample).

2.5. Statistical.

The statistical software Excel 2019 was used to calculate the main effects of the variables and their interactions and the data on the analysis of variance (ANOVA), with a level of significance of 90 %. The response surface methodology was used to optimize the conditions of synthesis. The Tukey test with \(p < 0.05\) was done. Graphical and statistical analyses were performed using Excel 2019.

3. Results and Discussion

3.1. Silver nanoparticles synthesis.

The decoded values of the experimental matrix are presented in Table 1. Parameters were subdivided within the chosen work range following the methodology of the CRCD. The size values, presented in the same table, are the mean of the nanostructure sizes with the highest percentage of distribution volume of the DLS replicates of each sample and their respective Polydispersity Index (PDI).

As the sizes of AgNP obtained varied from 14.08 to 157.60 nm, it confirms the synthesis of nanostructures, because to be considered nanostructure, the particles must have at least one of their dimensions in nanometric size and have a maximum of 100 nm for some authors and others, a maximum of 300 nm. However, the main characteristic of a nanostructure is that it presents a physical, chemical, or biological property different from that presented by its natural occurrence. The assays presented low values of PDI, with trials 1, 2, 3, 4, 5, 6, 15, and 16 showing the best values, below 0.4, indicating a good dispersion between the nanoparticles.

The ANOVA indicates that the temperature and stirring alone were significant parameters with a positive contribution to the tests with 90 % confidence. The F test also demonstrated the significance, the F value with 90 % was 2.06, and the F calculated with the values calculated by ANOVA was 15.01. So, the method is significant since the Fcalculated is higher than Ftabulated. Figure 1 shows the Pareto graph. Parameters that exceeded the line of the standardized t value were the agitation and temperature and the linear combinations between agitation and temperature, agitation and reagent flow, and temperature and reagent flow, all with 90 % significance. Therefore, the interactions of the factors are significant.
Stirring was the factor that most contributed to the synthesis of nanoparticles. The higher the stirring speed, the smaller the nanostructures sizes obtained. The energy provided by stirring prevents the aggregation of the molecules during the reaction and ensures greater homogeneity in the reaction medium. The temperature was significant, indicating that the synthesis of smaller nanostructures occurs at lower or higher temperatures. However, it is possible to obtain nanostructure even at moderate temperatures.

The linear relation between reagent flow and the temperature is observed in Figure 2. The working range of the temperature in that combination is reduced near the central point, which represents values close at 25 ºC, for any flow value indicating this as the best region for work.

The three surfaces allow the analysis to optimize the process, indicating which variables can be modified and the possible effects on AgNP formed.
Therefore, it was established that the chemical synthesis of AgNPs for applications in future works should occur at 25 °C. However, studies others show that, at 90 °C, it is possible to synthesize AgNPs with sizes between 5-50 nm, maintaining the vigorous stirring for 15 min and the AgNO₃ concentration of 1 mmol·L⁻¹[22]. We have obtained similar results, as described in Table 1.

![Figure 1](https://biointerfaceresearch.com/)

**Figure 1.** Transmission Electron Microscopy (TEM) images showing silver nanoparticles (AgNP) with mag 30,000 x and 100 nm scale.

However, the synthesis occurring at 30 °C does not demand energy expenditure with cooling or excessive heating in addition to being in the optimum working region. The established value for stirring was 250 rpm, promoting a vigorous stirring to prevent the ions from aggregating and reagent flow of 2.5 mL·min⁻¹, parameters selected because they were also in the optimal work region.

On these established optimal conditions, we synthesize the silver nanoparticles to be used in the coating of Tara Gum to preserve bananas. To record the formation of AgNPs, Figure 3 show the Transmission Electron Microscopy (TEM) with an increase of 140,000 X of AgNPs synthesized under the established conditions, indicating the formation of spherical
nanoparticles, well dispersed and having a size smaller than 100 nm. The spherical shape was verified in other methodologies using chemical or biological synthesis[23].

The DLS analysis showed a size of 20.08 ± 0.17 nm with a PDI of 0.321 ± 0.047. Similar results were observed in the TEM image: the first population with 13.345 nm and 2nd population with 1.658 nm. The difference in the size measured by the two techniques occurs because in the DLS, the hydrodynamic radius is measured, and in the MET the sample is a dry structure[21]. The measured zeta potential was -31.3 ± 0.7, indicating that the system is stable. The negative value of the zeta potential can be explained by the presence of ionic salts used in the synthesis. The high value of zeta is important because it indicates good physical-chemical stability in the system, which prevents the aggregation of nanoparticles and changes in the properties of the system [24].

3.2. Nanocomposite rheological characteristics.

The rheological behavior was carried out on the rheometer at different temperatures. According to Figure 3A, an increase in temperature decreases the viscosity for the same rotation.

![Figure 4. Curves of the rheological behavior of the Tara Gum coating (1.5 % solution (w/v)) with Silver Nanoparticle. A) Behavior with temperature variation. B) Control, only 1.5 % Tara Gum (w/v). C) Tara Gum with 1 % (v/v) AgNP. D) Tara Gum with 3% (v/v) AgNP. E) Tara Gum with 5% (v/v) AgNP.]

This phenomenon occurs because the increase in temperature disrupts weaker intermolecular interactions, such as the interaction of Van der Waals and hydrogen bonds, leaving the medium more fluid, so at higher temperatures, the Tara Gum solution has Newtonian behavior.
For comparison between samples, a temperature of 30 ºC was chosen. In Figures 4 (B-E) can be seen that the up curve and the down curve were superimposed. Therefore, the fluid is pseudoplastic. This behavior occurred for the control and the other samples, indicating that the addition of AgNP did not change the rheological behavior. It may be related to the fact that AgNPs are smaller than galactomannan molecules and were used in low concentrations. Maintaining the rheological characteristics facilitates industrial application in tare gum as a fruit coating. The results obtained in this work are similar to the ones obtained by Kim and Yoo (2009) [25], who concluded that the Tara Gum solution is a pseudoplastic fluid, and the increased concentration of Tara Gum leaves the pseudoplastic behavior of the fluid more pronounced. Santos et al. (2019) also found a pseudoplastic behavior for the Tara Gum solution [26].

3.3. Banana analyses.

Table 2 shows the banana cv. Caturra fresh weight loss after 14 days of storage. The average weight loss percentage varied between 19-22 % among all subgroups. Since there is no difference between the averages, it can be said that the Tara gum coating did not delay the transfer of water from the fruit. Figure 5 shows the firmness reduction after 14 days of storage. There was a difference between the coated samples and the control. It is possible to compare the results of different nanostructure concentrations. On the last day of analyses, the 5 % AgNP (w/v) coating demonstrated excellent efficiency, positively influencing the fruit mechanical resistance, while the control showed a lower toughness value.

Different firmness values can be caused by the decrease in elasticity and viscosity of the fruit, syntheses reactions, as hydrolysis of starch, cellular wall components degradation, and cell turgescence loss with consequence ripening advance [27,28]. Thus, it is suggested that the direct contact of the coating with the banana peel allowed changes in the metabolic activity; it is observed that the higher the concentration of silver nanoparticles, the greater is the coating efficiency. In this way, this concentration of Silver Nanoparticles with Tara Gum can slow up the transpiration process and fruit senescence.

Figure 6a shows the hue angle of bananas, and it is observed that on the second day, bananas from all subgroups had values close to each other and close to 120 °, thereby, all green. On the eighth day of storage, there is a decline in the hue angle value, which indicates that the bananas have yellow-green tones. The most significant difference is on the 14th day, in which the bananas of the control subgroup showed a hue angle with a mean much less than 90 °, while bananas treated with Tara gum, with and without nanosilver, were maintained values above 90 °. It means that bananas without treatment on the 14th day showed a black color, indicating an advanced stage of putrefaction. This behavior is observed in Figure 4b, in which the bananas are illustrated in the respective storage days analyzed.

The Tara gum coating is efficient in controlling the color change of the banana, in addition to inferring a shinier aspect to the fruit, a factor that directly impacts consumption. The difference in AgNP concentration did not influence the result.
Table 2. Physical-chemical analysis of bananas cv. Caturra coated with Tara gum with different concentrations of silver nanoparticles stored for 14 days. The bananas were evaluated in fresh weight loss, malic acid percentage of Total Titratable Acid (TTA), and Total Soluble Solids (TSS) expressed in ºBrix. Tukey Test with 0.05 of reliability*.

| Treatment          | Day 2 |          |          |          | Day 8 |          |          |          | Day 14 |          |
|--------------------|-------|----------|----------|----------|-------|----------|----------|----------|--------|----------|
|                    | Weight loss | TTA      | TSS      | Weight loss | TTA      | TSS      | Weight loss | TTA      | TSS    |          |
| Control            | 4.36 ± 0.19aa | 0.1712 ± 0.028aa | 14.92 ± 0.29aa | 14.13 ± 1.79ab | 29.92 ± 0.35aa | 21.87 ± 4.65ab | 0.2122 ± 0.011aa | 63.93 ± 0.58ab |
| Tara Gum           | 3.31 ± 0.31aa | 0.2084 ± 0.021aa | 14.92 ± 0.29aa | 11.00 ± 0.68ab | 0.3648 ± 0.042ab | 23.92 ± 2.47ab | 18.63 ± 1.90ab | 0.2754 ± 0.046ab | 32.92 ± 2.02ab |
| TG + 1% AgNP       | 3.70 ± 0.34aa | 0.2159 ± 0.028aa | 13.92 ± 0.00aa | 10.47 ± 0.38ab | 0.1936 ± 0.021ab | 30.29 ± 0.29a | 21.44 ± 1.28aC | 0.2829 ± 0.074a | 50.92 ± 2.25ab |
| TG + 3% AgNP       | 3.04 ± 0.39aa | 0.1936 ± 0.028aa | 13.92 ± 0.00aa | 10.78 ± 0.50ab | 0.201 ± 0.018ab | 34.92 ± 0.58a | 19.73 ± 1.01aC | 0.3648 ± 0.042ab | 44.92 ± 3.00ab |
| TG + 5% AgNP       | 3.37 ± 0.11aa | 0.1787 ± 0.018aa | 13.92 ± 0.00aa | 10.84 ± 1.25ab | 0.2308 ± 0.038ab | 40.92 ± 0.71a | 19.64 ± 1.77ab | 0.2829 ± 0.011ab | 13.92 ± 0.00ab |

*Lowercase refers to the column, and uppercase refers to the line. Statistical analyses were made for each test.

Figure 5. Firmness values of bananas submitted to Tara Gum integrated with different nanosilver concentrations for 14 days. Tukey Test (p < 0.05) was represented with lowercase referring to each day and uppcases for each treatment.
However, it is possible to observe that the coating of Tara Gum with AgNP modifies the atmosphere of the fruit, controlling the mass transfer of oxygen and water, which causes changes in the metabolic activities of the fruit [27,29].

Thus, bananas treated with Tara gum with and without silver nanoparticles maintained their yellow-green color. The bananas without coating treatment indicated brown colors; this happens because of the additional maturation reaction caused by polyphenol oxidase, which polymerizes macromolecules responsible for color changes [30].

Figure 4. Color variation of banana peels is represented by: A) Graph of Hue angle curves (H°) comparing the behavior of the shade variation during days 0, 8, and 14. The ■ symbol represents the control subgroup, the ● symbol represents the Tara Gum subgroup, the ▲ symbol represents 1% AgNP subgroup, the ▲ symbol represents 3% AgNP subgroup, and ♦ symbol represents 5% AgNP subgroup. B) Photos of bananas from all subgroups on days 0, 8, and 14, indicating the behavior of the mean of their values of L*a*b*.
There was no expressive pH variation after 14 days, with values between 5.3 to 5.9, but without a significant difference in the applied coatings. Differently, Gol and Rao (2011) observed a higher pH value for the control sample compared with a coated banana using chitosan [31]. There are three important acids present in bananas. Malic acid and citric acid are responsible for the sour flavor of green bananas, and oxalic acid is responsible for astringency [13,29]. Table 2 shows Total Titratable Acid (TTA) values. All fruits in the study had an increase in the percentage of malic acid for 14 days in all coatings submitted, having the coating with Tara gum integrated with 3 % of AgNP the most expressive value, with an increase of 88.43 % in terms of acid malic. In contradiction, the control sample presented an increase of 23.95 %. The increase in acidity happens in the first week of storage, as described by Thakur et al. (2019) that AT up from 0.15 % on day one to 0.37 % on day 4 using starch coating on banana [13]. Kittur et al. (2014) observed that bananas treated with polysaccharides were lower in titratable acidity than the control fruits [32].

Another fruit maturation stage indicator is Total Soluble Solids (TSS), representing soluble compounds in fruits, such as vitamins, sugars, acids, amino acids, and pectin. The value usually increases with the ripening. Table 2 shows °Brix values for samples with different coatings. From that, is possible to verify the increase of TSS in 8 and 14 days. Statistically, on the last day, the coating with higher AgNP concentration kept the same as the beginning. TSS value rises during ripening in all cases. The control sample had an increase of more than 23% in terms of °Brix. The 5 % AgNP + TG coating was capable of maintaining the same value over the ripening so that this coating can slow down the banana metabolism. In other words, the coating of Tara Gum with Silver Nanoparticles was capable of slowing the increase in TSS value in 14 days, ensuring its efficiency as protecting coating for fruits.

This suggests that the coating with AgNP is less permeable to water and air, changing the external conditions of the banana that impact physiological behavior [31,32]. An increase also is shown in banana TSS value by Soltani et al. (2011) [33], from 7.8 to 18.6 °Brix. A carriage coating was developed by Dwivany et al. (2020) [34], which observed the TSS for a banana at the control group increased until 11 days, then decreased. When the carrageenan coating was applied at concentrations 0.5 % and 0.1 %, TSS increased faster. On the other hand, the 1.5 % concentration of the coating provided a smaller increase in total solids.

4. Conclusions

The response surface methodology provided satisfactory results for optimizing aqueous silver nanoparticle chemical synthesis, showing the optimal regions to obtain nanostructures of small sizes, which can be performed at 25 ºC under the agitation of 250 rpm and flow of 2.5 mL·min⁻¹. Samples submitted to the coating of Tara Gum with a greater concentration of Silver Nanoparticles (5%) showed the best result, with a color closer to the initial stage, less weight loss, higher firmness, lower value of soluble solids, and lower Ripening Index. All this information proves the efficiency of Silver Nanoparticles when integrated into Tara Gum as a coating with the capability of protection and shelf-life extension of fruits. Due to its application viability and verified results, the coating produced has a huge potential for real utilization in the food industry, competing directly with traditional coatings.

Funding

This research received no external funding.
Acknowledgments

The authors thank CNPq for financial support, to UFOP CiPharma multiuser laboratory for measures in NanoZeta Sizer, with the project "Asymmetric Flow Field Flow Fractionation" (FAPEMIG CDS – APQ 01510-14), and to the Laboratory of Technology of Packaging of UFSJ – Sete Lagoas. This research used facilities of the Brazilian Nanotechnology National Laboratory (LNNano), part of the Brazilian Centre for Research in Energy and Materials (CNPEM), a private non-profit organization under the supervision of the Brazilian Ministry for Science, Technology, and Innovations (MCTI). The TEM-EL staff is acknowledged for their assistance during the experiments (TEM-C2-25381).

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Sagar, N.A.; Pareek, S.; Sharma, S.; Yahia, E.M.; Lobo, M.G. Fruit and Vegetable Waste: Bioactive Compounds, Their Extraction, and Possible Utilization. Comprehensive Reviews in Food Science and Food Safety 2018, 17, 512–531, https://doi.org/10.1111/1541-4337.12330.
2. Elik, A.; Yanik, D.K.; Yanik, D.K.; Guzelsoy, N.A.; Yavuz, A.; Gogus, F. Strategies to Reduce Post-Harvest Losses for Fruits and Vegetables Innovative Mild Processing Tailored to Ensure Sustainable and High-Quality Organic Fruit Products-MILDSUSFRUIT-ERA NET Project View Project "Enhancing Youth Employability in Bakery Sector" View Project Strategies to Reduce Post-Harvest Losses for Fruits and Vegetables., https://doi.org/10.7176/JSTR/5-3-04.
3. Nair, M.S.; Tomar, M.; Punia, S.; Kukula-Koch, W.; Kumar, M. Enhancing the Functionality of Chitosan-and Alginate-Based Active Edible Coatings/Films for the Preservation of Fruits and Vegetables: A Review. International Journal of Biological Macromolecules 2020, 164, 304–320, https://doi.org/10.1016/J.IJBIOMAC.2020.07.083.
4. Panahirad, S.; Dadpour, M.; Peighambardoust, S.H.; Soltanzadeh, M.; Gullón, B.; Alirezalu, K.; Lorenzo, J.M. Applications of Carboxymethyl Cellulose- and Pectin-Based Active Edible Coatings/Films for the Preservation of Fruits and Vegetables: A Review. Trends in Food Science & Technology 2021, 110, 663–673, https://doi.org/10.1016/J.TIFS.2021.02.025.
5. Zambrano-Zaragoza, M.L.; González-Reza, R.; Mendoza-Muñoz, N.; Miranda-Linares, V.; Bernal-Couoh, T.F.; Mendoza-Elvira, S.; Quintanar-Guerrero, D. Nanosystems in Edible Coatings: A Novel Strategy for Food Preservation. International Journal of Molecular Sciences 2018,19, 705, 2018, 19, 705, https://doi.org/10.3390/IJMS19030705.
6. Anupam Roy; Onur Bulut; Sudip Some; Kumar Mandal, A.; Deniz Yilmaz, M. Green Synthesis of Silver Nanoparticles: Biomolecule-Nanoparticle Organizations Targeting Antimicrobial Activity. RSC Advances 2019, 9, 2673–2702, https://doi.org/10.1039/C8RA08982E.
7. Tortella, G.R.; Rubilar, O.; Durán, N.; Diez, M.C.; Martínez, M.; Parada, J.; Seabra, A.B. Silver Nanoparticles: Toxicity in Model Organisms as an Overview of Its Hazard for Human Health and the Environment. Journal of Hazardous Materials 2020, 390, 121974, https://doi.org/10.1016/J.JHAZMAT.2019.121974.
8. Kraśniewska, K.; Galus, S.; Gniewosz, M. Biopolymers-Based Materials Containing Silver Nanoparticles as Active Packaging for Food Applications–A Review. International Journal of Molecular Sciences 2020, 21, 698, 2020, 21, 698, https://doi.org/10.3390/IJMS21030698.
9. Khezerlou, A.; Zolfaghari, H.; Banihashemi, S.A.; Forghani, S.; Ehsani, A. Plant Gums as the Functional Compounds for Edible Films and Coatings in the Food Industry: A Review. Polymers for Advanced Technologies 2021, 32, 2306–2326, https://doi.org/10.1002/PAT.5293.
10. Salehi, F. Edible Coating of Fruits and Vegetables Using Natural Gums: A Review. 2020, 20, S570–S589, https://doi.org/10.1080/15538362.2020.1746730. , https://doi.org/10.1080/15538362.2020.1746730.
11. Pellá, M.C.G.; Silva, O.A.; Pellá, M.G.; Beneton, A.G.; Caetano, J.; Simões, M.R.; Dragunski, D.C. Effect of Gelatin and Casein Additions on Starch Edible Biodegradable Films for Fruit Surface Coating. *Food Chemistry* 2020, 309, 125764, https://doi.org/10.1016/J.FOODCHEM.2019.125764.

12. Shah, S.; Hashmi, M.S. Chitosan–Aloe Vera Gel Coating Delays Postharvest Decay of Mango Fruit. *Horticulture, Environment, and Biotechnology* 2020 61:2 2020, 61, 279–289, https://doi.org/10.1007/S13580-019-00224-7.

13. Thakur, R.; Pritistijono, P.; Bowyer, M.; Singh, S.P.; Scarlett, C.J.; Stathopoulos, C.E.; Vuong, Q. v. A Starch Edible Surface Coating Delays Banana Fruit Ripening. *LWT* 2019, 100, 341–347, https://doi.org/10.1016/J.LWT.2018.10.055.

14. Liu, F.; Chang, W.; Chen, M.; Xu, F.; Ma, J.; Zhong, F. Film-Forming Properties of Guar Gum, Tara Gum and Locust Bean Gum. *Food Hydrocolloids* 2020, 98, 105007, https://doi.org/10.1016/J.FOODHYD.2019.03.028.

15. Liu, F.; Chang, W.; Chen, M.; Xu, F.; Ma, J.; Zhong, F. Film-Forming Properties of Guar Gum, Tara Gum and Locust Bean Gum. *Food Hydrocolloids* 2020, 98, 105007, https://doi.org/10.1016/J.FOODHYD.2019.03.028.

16. Yu, Z.; Wang, W.; Kong, F.; Lin, M.; Mustapha, A. Cellulose Nanofibril/Silver Nanoparticle Composite as an Active Food Packaging System and Its Toxicity to Human Colon Cells. *International Journal of Biological Macromolecules* 2019, 129, 887–894, https://doi.org/10.1016/J.IJBIOMAC.2019.02.084.

17. Raza, M.A.; Kanwal, Z.; Rauf, A.; Sabri, A.N.; Riaz, S.; Naseem, S. Size- and Shape-Dependent Antibacterial Studies of Silver Nanoparticles Synthesized by Wet Chemical Routes. *Nanomaterials* 2016, 6, 74, https://doi.org/10.3390/NANO6040074.

18. Marichamy, S.; Stalin, B.; Ravichandran, M.; Sudha, G.T. Optimization of Machining Parameters of EDM for α-β Brass Using Response Surface Methodology. *Materials Today: Proceedings* 2020, 24, 1400–1409, https://doi.org/10.1016/J.MATPR.2020.04.458.

19. Peng, X.; Yang, G.; Shi, Y.; Zhou, Y.; Zhang, M.; Li, S. Box–Behnken Design Based Statistical Modeling for the Extraction and Physicochemical Properties of Pectin from Sunflower Heads and the Comparison with Commercial Low-Methoxyl Pectin. *Scientific Reports* 2020 10:1 2020, 10, 1–10, https://doi.org/10.1038/s41598-020-60339-1.

20. Yam, K.L.; Papadakis, S.E. A Simple Digital Imaging Method for Measuring and Analyzing Color of Food Surfaces. *Journal of Food Engineering* 2004, 61, 137–142, https://doi.org/10.1016/S0260-8774(03)00195-X.

21. Souza, V.A.B. de; Byrne, D.H.; Taylor, J.F. Heritability, Genetic and Phenotypic Correlations, and Predicted Selection Response of Quantitative Traits in Peach: II. An Analysis of Several Fruit Traits. *Journal of the American Society for Horticultural Science* 1998, 123, 604–611, https://doi.org/10.21273/JASHS.123.4.604.

22. Chowdhury, S.; Yusof, F.; Faruck, M.O.; Sulaiman, N. Process Optimization of Silver Nanoparticle Synthesis Using Response Surface Methodology. *Procedia Engineering* 2016, 148, 992–999, https://doi.org/10.1016/J.PROENG.2016.06.552.

23. Jayeoye, T.J.; Nwabor, O.F.; Rujirailai, T. Synthesis of Highly Stable and Dispersed Silver Nanoparticles/Poly(Vinyl Alcohol-Co-Ethylene Glycol)/Poly(3-Aminophenyl Boronic Acid) Nanocomposite: Characterization and Antibacterial, Hemolytic and Cytotoxicity Studies. *Journal of Industrial and Engineering Chemistry* 2020, 89, 288–300, https://doi.org/10.1016/J.JIEC.2020.05.025.

24. Machado, G.T.P.; Veleirinho, M.B.; Mazzarino, L.; Filho, L.C.P.M.; Maraschin, M.; Cerri, R.L.A.; Kuhnenn, S. Development of Propolis Nanoparticles for the Treatment of Bovine Mastitis: In Vitro Studies on Antimicrobial and Cytotoxic Activities. https://doi.org/10.1139/cjas-2018-0173. 2019, 99, 713–723, https://doi.org/10.1139/CJAS-2018-0173.

25. Kim, W.-W.; Yoo, B. Rheological Behaviour of Acorn Starch Dispersions: Effects of Concentration and Temperature. *International Journal of Food Science & Technology* 2009, 44, 503–509, https://doi.org/10.1111/J.1365-2621.2008.01760.X.

26. Santos, M.B.; dos Santos, C.H.C.; de Carvalho, M.G.; de Carvalho, C.W.P.; Garcia-Rojas, E.E. Physicochemical, Thermal and Rheological Properties of Synthesized Carboxymethyl Tara Gum (Caesalpinia Spinosa). *International Journal of Biological Macromolecules* 2019, 134, 595–603, https://doi.org/10.1016/J.IJBIOMAC.2019.05.025.

27. Shi, Z.; Yang, H.; Jiao, J.; Wang, F.; Lu, Y.; Deng, J. Effects of Graft Copolymer of Chitosan and Salicylic Acid on Reducing Rot of Postharvest Fruit and Retarding Cell Wall Degradation in Grapefruit during Storage. *Food Chemistry* 2019, 283, 92–100, https://doi.org/10.1016/J.FOODCHEM.2018.12.078.
28. Marín-Rodríguez, M.C.; Orchard, J.; Seymour, G.B. Pectate Lyases, Cell Wall Degradation and Fruit Softening. *Journal of Experimental Botany* 2002, 53, 2115–2119, https://doi.org/10.1093/JXB/ERF089.

29. Huang, H.; Jing, G.; Guo, L.; Zhang, D.; Yang, B.; Duan, X.; Ashraf, M.; Jiang, Y. Effect of Oxalic Acid on Ripening Attributes of Banana Fruit during Storage. *Postharvest Biology and Technology* 2013, 84, 22–27, https://doi.org/10.1016/J.POSTHARVBIO.2013.04.002.

30. La, D.D.; Nguyen-Tri, P.; Le, K.H.; Nguyen, P.T.M.; Nguyen, M.D.B.; Vo, A.T.K.; Nguyen, M.T.H.; Chang, S.W.; Tran, L.D.; Chung, W.J.; et al. Effects of Antibacterial ZnO Nanoparticles on the Performance of a Chitosan/Gum Arabic Edible Coating for Post-Harvest Banana Preservation. *Progress in Organic Coatings* 2021, 151, 106057, https://doi.org/10.1016/J.PORGCOAT.2020.106057.

31. Gol, N.B.; Rao, T.V.R. Banana Fruit Ripening as Influenced by Edible Coatings. 2011, 11, 119–135, https://doi.org/10.1080/15538362.2011.578512.

32. Kittur, F.; Saroja, N.; Habibunnisa; Tharanathan, R. Polysaccharide-Based Composite Coating Formulations for Shelf-Life Extension of Fresh Banana and Mango. *European Food Research and Technology* 2001 213:4 2014, 213, 306–311, https://doi.org/10.1007/S002170100363.

33. Soltani, M.; Alimardani, R.; Omid, M. Evaluating Banana Ripening Status from Measuring Dielectric Properties. *Journal of Food Engineering* 2011, 105, 625–631, https://doi.org/10.1016/J.JFOODENG.2011.03.032.

34. Dwivany, F.M.; Apriyandi, A.N.; Suendo, V.; Sukriandi, N. Carrageenan Edible Coating Application Prolongs Cavendish Banana Shelf Life. *International Journal of Food Science* 2020, 2020, https://doi.org/10.1155/2020/8861610.