Synthesis and characterization of starch stabilized Ag nanoparticles. Effect of the crystalline structure of starch.

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Abstract. Silver nanoparticles (AgNps) are known for their antimicrobial activity and other physicochemical properties that can be applied in several fields. Most of their synthesis methods include chemical reduction and the use of stabilizing agents such as starch. In recent years, several green methods have been developed such as using carbohydrates as reducing agents. On the other hand, starch is a semi crystalline structure formed by mixtures of the linear glucan, amylase and the branched glucon amylopectin. In this work we studied the effect of the semi crystalline structure on the physicochemical properties (particle size and surface plasmon resonance). Three types of starch were selected (corn, potato and banana) representing the three types of semi crystalline structures of the starch granule (A, B and C). Results showed that banana starch allowed larger particle sizes and broader size distribution, while there was not significant difference between nanoparticles stabilized with A and B type starches.

1. Introduction

Silver nanoparticles (AgNps) are among the most studied and most interesting nanomateriales, as they have shown very unique and attractive physical, chemical and biological properties, which can be used in several applications such as antimicrobial agents, anticancer medicines, electronic devices and waste water treatment. One of the most common methods for AgNps synthesis is the chemical reduction of silver ions in aqueous or organic solvent solutions, forming a stable colloidal dispersions by using reducing agents such as borohydride, citrate, ascorbate, and elemental hydrogen. However, several new reducing agents have been used in order to have a greener approach to AgNps synthesis, including sugars, plant extracts, essential oils, and hydrothermal methods.

Starch is considered the second most common biopolymer on earth, as it is used by plants as an energy reserve and can be found in roots, leaves and fruits. Starch forms granules of different morphologies depending of the botanical origin and growth conditions. Starch structure is formed by to types of glucosides, the linear amylase and the branched amylopectin formed by glucose molecules linked by 1,6-α and 1,4-α linkages. Both molecules are distributed through the starch granules, forming crystalline and amorphous regions along the granule. Due to their semi-crystalline...
structure, starch granules can be studied by using X-ray diffraction (XRD), and according to their XRD diffraction pattern starches can be classified into three crystalline types called A, B, and C. (12, 13)

In recent years several authors have reported that starch can be used as a stabilizing agent in green synthesis of AgNps, increasing their stability while maintaining their physicochemical and antimicrobial properties, however, only one type of starch is commonly used. (14, 15) In this paper, we studied the effect of the semi-crystalline structure of starch in the structure and physicochemical properties of AgNps synthetized using glucose as a reducing agent.

2. Experimental methods

2.1. Materials

Potato and corn starch were purchased from Sigma (St. Louis, MO, USA), and banana starch was extracted from green bananas of the FHIA 21 variety according to the methodology described by Santoyo-Aleman, et al. (16). D-(+) glucose, analytical grade silver nitrate and sodium hydroxide were purchased from Sigma (St. Louis, MO, USA). All other regents used in this study were analytical grade and purchased from Sigma (St. Louis, MO, USA).

2.2. Starch coated-AgNps synthesis.

Starch coated—AgNps (S-AgNps) were synthetized according to the method proposed by Vasileva, et al, (17) with some modifications. In brief, a determinate amount of starch was dispersed in 32 mL of water in order to obtain a 0.2% dispersion by using a magnetic stirrer (600 rpm). Then, 16 mL of a 1x10^{-3} M AgNO\textsubscript{3} solution, the mixture was continuously stirred for 10 minutes and after that, 480 μL of a 1 M D-(+) glucose aqueous solution were added as a reducing agent. Finally, 2.4 mL of NaOH (0.1 M) were added and the colloidal dispersion was stirred during 30 minutes at 600 rpm.

2.3 Starch characterization

X-ray diffraction (XRD) spectroscopy analyses were carried out in a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 100 m\text{A} with a Cu-K\text{α} radiation (\lambda = 1.54 Å. All samples were scanned through the 2θ range of 5 – 40°, with a continuous scan mode at room temperature.

Amylose and amylopectin content were determined according by using a colorimetric method described by Eggleston, et al. (18)

2.4 S-AgNps characterization.

Particle size and polydispersity index (in aqueous solution were measured by dynamic light scattering using a Mastersizer 2000 (Malvern) system. The suspensions were diluted with distilled water to a concentration of about 0.01%. The mean particle size and the polydispersity index (Pdi) are reported.

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Absorption spectra of the S-AgNPs colloidal dispersions were recorded by using Hewlett Packard UV-Vis spectrophotometer (HP-8453). A silverless starch solution was used as a reference sample for background absorption in all measurements.

3. Results and analysis.

3.1 Starch characterization.

As mentioned in the introduction one of the main characteristics of starch is its semicristalyne structure, formed by the distribution of the linear amylose and the highly branched amylopectin through the granule. Figure 1 shows the X-ray diffraction pattern of corn, potato and banana starch, while Table 1, shows the amylose and amylopectin content of those three types of starch.

![X-Ray diffraction patterns of corn, potato and banana starch.](image)

Table 1. Amylose content, amylopectin content and relative cristalinity (RC) of corn, potato and banana starch.

| Starch Type | Amylose (%) | Amylopectin (%) | RC (%) |
|-------------|-------------|-----------------|-------|
| Corn        | 28.3        | 71.7            | 21.2  |
| Potato      | 24.5        | 75.5            | 24.3  |
| Banana      | 30.1        | 69.9            | 20.5  |
As shown in Figure 1, all three starches showed a broad amorphous region with broad crystalline peaks. Corn starch diffraction pattern presented the typical peaks assigned to an A-type starch ($2\theta = 15^\circ$, $17^\circ$, $18^\circ$ and $23^\circ$. On the other hand, potato starch showed peaks at $2\theta = 5^\circ$ and $17^\circ$, characteristic of B-type starches. Finally, banana starch presented peaks of both A-type and B-type starches, attributed to C-type starches. Table 1, shows that all three starch have a similar amylose content, ranging from 24.5% for potato starch to 30.1% for banana starch. Furthermore, Table 1 also shows that relative crystallinity is related to amylose content, as banana starch has the higher amylose content, thus a bigger amorphous region.

3.2 S-AgNps Characterization.

All S-AgNps suspensions showed the yellowish color of the surface resonance plasmon of silver nanoparticles, indicating that the different types of starch did not affect the reduction of Ag$^{+1}$ ions into nanoparticles. Furthermore, visual inspection of all colloidal suspensions up to twelve weeks, did not show any significant changes, indicating great stability provided by the starch molecules. Figure 2 shows the UV-Vis spectra and picture of the S-AgNps. UV-Vis spectra maxima and full width half maxima (FWHM) change between the three starch types, as shown in Table 2.

![Figure 2](image-url)

**Figure 2.** (I) UV-Vis spectra of the different S-AgNps synthetized and (II) pictures o A) AgNps; B) Banana S-AgNps; C) Corn S-AgNps; D) Cassava S-AgNps.
Table 2. UV-Vis maxima, fill width half maxima (FWHM), particle size and polidispersity of S-AgNPs using different types of starch.

| Starch type | UV-Vis maxima (nm) | FWHM (nm) | Particle Size (nm) | Polidispersity |
|-------------|------------------|-----------|-------------------|----------------|
| Corn        | 405              | 54        | 15.4              | 0.123          |
| Potato      | 408              | 60        | 17.5              | 0.091          |
| Banana      | 412              | 71        | 39.1              | 0.153          |

S-AgNps made with corn starch presented the narrowest band, with a peak a 405 nm this values were similar to the ones obtained for potato starch S-AgNps with maxima at 408 nm and a FWHM of 60 nm. On the other hand, S-AgNps, obtained from banana starch showed maxima at 412 nm and a broader band with FWHM values of 71 nm. It is known, that surface resonance plasmon maxima is heavily dependent of the nanoparticles size with bathochromic shifts as particles size is increased, indicating that banana starch S-AgNps presented a bigger size than other starches. Furthermore, a narrower band is an indicator of the formation of uniform spherical nanoparticles. This is further confirmed by DLS studies shown in Table 2, with corn and potato S-AgNps presenting smaller particle size and lower polidispersity than banana S-AgNps.

4. Conclusion

Results showed that banana starch allowed larger particle sizes and broader size distribution, while there was not significant difference between nanoparticles stabilized with A and B type starches. It seems that only C type starches have a significant effect on the physicochemical properties of the silver nanoparticles, however, this can also be attributed to their bigger amylose content and granule size, so further studies are needed.

5. Acknowledgments

The authors want to thank the Vicerrectoria de Investigaciones, Facultad de Ciencias Básicas y Tecnologías, Facultad de Ciencias Agroindustriales, Programa de Quimica, Programa de Ingeniería de Alimentos and FEDEPLATANO for their support.

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