GOLD NANOPARTICLES SYNTHESIS WITH DIFFERENT REDUCING AGENTS CHARACTERIZED BY UV-VISIBLE ESPECTROSCOPY AND FTIR

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Abstract
This study aims to analyze the syntheses of gold nanoparticles with different reducing agents: Sodium Citrate and Sodium Borohydride. The syntheses were characterized by Ultraviolet-visible Spectroscopy and the Fourier Transform Infrared Spectroscopy, in which we evaluated the influence of the reducing agent and the reaction agitation. The test results indicated the presence of metallic gold and confirmed the formation of gold nanoparticles. Finally, we composed a table showing the differences between the characteristics of the two reducing agents.

Keywords: Gold, Nanoparticles, Reducing, Characterization, Tests.

SÍNTESE DE NANOPARTÍCULAS DE OURO COM DIFERENTES AGENTES REDUTORES CARACTERIZADA POR ESPECTROSCOPIA UV-VISÍVEL E FTIR

Resumo

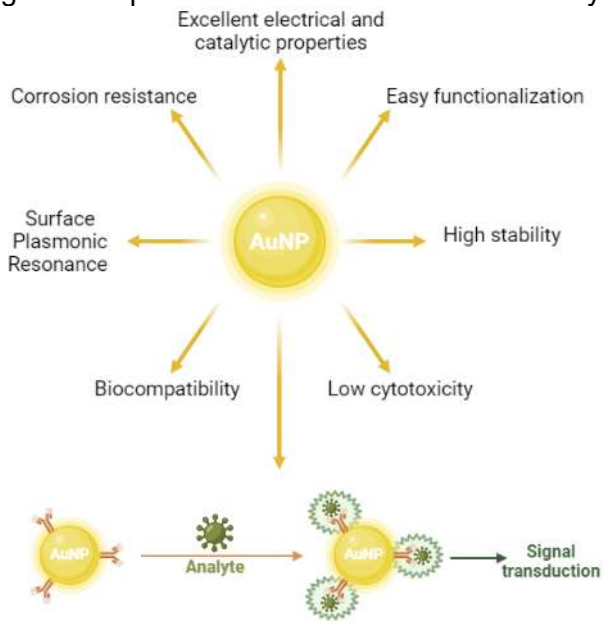
O presente estudo tem como objetivo analisar a síntese de nanopartículas de ouro realizada com diferentes agentes redutores: Citrato de Sódio e Borohidreto de Sódio. As sínteses foram caracterizadas através das análises de Espectroscopia Ultravioleta-visível e Espectroscopia no Infravermelho por Transformada de Fourier, onde foi avaliada a influência do agente redutor e da agitação da reação nas características das soluções coloidais produzidas. Os resultados dos testes indicaram a presença de ouro metálico e confirmaram a formação de nanopartículas de ouro. Por fim, foi elaborada uma tabela mostrando as diferenças entre as características dos dois agentes redutores.

Palavras-chave: Ouro, Nanopartículas, Redução, Caracterização, Testes.

1. INTRODUCTION

Nanomaterials are classified as such if at least one of their dimensions is between 1 and 100 nm. They have unique chemical and physical properties in terms of shape, size, distribution, crystallinity, agglomeration state, and morphology [1], which make them suitable for use in various segments, including the cosmetic, chemical, food, and feed industries; in the manufacture of electronic components; in the synthesis of polymeric and pigment nanocomposites; in the design of devices for the detection of diseases, alternative mechanisms for drug and gene delivery [1,2]. For biomedical applications, one of the most explored nanomaterials is gold nanoparticles (AuNPs) as they have excellent electrical and catalytic properties, corrosion resistance, surface plasmonic resonance properties (SPR), intrinsic biocompatibility, low cytotoxicity, high stability in biological fluids, and easy functionalization with biological species of interest [2,3]. Figure 1 summarizes the characteristics of AuNPs and a simplified scheme of how biomolecules using these nanoparticles are detected.

Figure 1. Properties of gold nanoparticles and schematic detection system based on AuNPs



One of the most consolidated methodologies for gold nanoparticles synthesis is the chemical reduction of Au^{3+} ions, present in precursors such as Chloroauric Acid, in metallic gold, through reducing agents such as Sodium Citrate [4] and Sodium Borohydride [5]. The chemically synthesized gold nanoparticles are dispersed in a liquid medium, producing a colloidal solution that can have different colors depending on the size of these nanoparticles. The change in the synthesis parameters influences the shape and size of the nanoparticles, interfering, consequently, in their application. This work aimed to study the gold nanoparticles process synthesis through the chemical reduction method, in which we evaluated the influence of the reducing agent and the reaction agitation rate.

2. METHODOLOGY

To produce the gold nanoparticles, Anhydrous Sodium Citrate (Na3C6H5O7) from VETEC and Sodium Borohydride ($NaBH_4$) from Sigma-Aldrich were used as reducing agents; Chloroauric Acid trihydrate ($HAuCl_4.3H_2O$) purchased from Synth was used as gold precursor; Polyvinylpyrrolidone (PVP) with 10,000 g/mol from Sigma-

Aldrich was used as a stabilizer; and ultrapure water, as solvent. Initially, all glassware was washed with aqua regia, prepared by a mixture of Nitric Acid (65%) and Hydrochloric Acid (37%) purchased from Química Moderna in volume ratio 1:4, for the complete cleaning and elimination of possible contaminations.

2.1. Chemical Reduction via Sodium Citrate

The experimental procedure described in this section was based on the formation of gold nanoparticles through the chemical reduction of gold ions into metallic gold using Sodium Citrate that acts both as a reducing agent and as a stabilizer of AuNPs, preventing their agglomeration [4]. In 95 mL of ultrapure water, approximately 15 mg of Chloroauric Acid was added, under constant stirring and heating (90°C). Simultaneously, 5 mL of a Sodium Citrate solution (10 mg/mL) was dropping into the Chloroauric Acid solution (1 drop/s). The system remained under constant heating and stirring for another 20 minutes. Finally, the solution was kept at rest, at room temperature, for its gradual cooling and stored in a refrigerator (± 5 ºC). The influence of the stirring speed on the characteristic of the colloidal solution was analyzed, thus, six samples were synthesized with the following stirring speeds: 250 rpm, 500 rpm, 750 rpm, 1,000 rpm, 1,250 rpm, and 1,500 rpm.

2.2. Chemical Reduction via Sodium Borohydride

The experimental procedure detailed here was based on the synthesis of gold nanoparticles by chemical reduction via Sodium Borohydride using Polyvinylpyrrolidone as a stabilizing reagent [6]. Approximately 25 mg of Chloroauric Acid and 60 mL of ultrapure water were added to a beaker, under constant stirring. Subsequently, 10 mg of PVP was gradually added to the solution, accompanied by another 35 mL of ultrapure water and the system was kept under agitation for 30 min. Then, 5 mL of an aqueous solution of Sodium Borohydride, containing 1 mmol of the reducing agent, was added. The system was kept under agitation for another 1 hour. Finally, the solution was stored in a refrigerator (± 5 ºC). Similar to the study developed with Sodium Citrate, two stirring speeds were evaluated: 750 rpm and 1,500 rpm.

2.3. Characterization

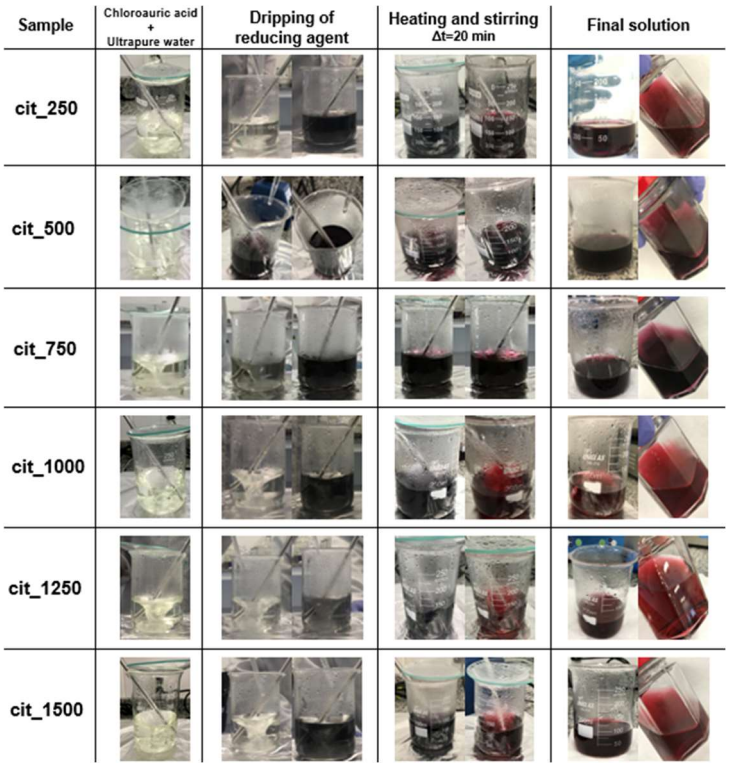
The solutions of gold nanoparticles synthesized were evaluated through the analysis of Ultraviolet-visible (UV-vis) Spectroscopy carried out in a Shimadzu UV-2600 spectrophotometer, using plastic cuvettes of 4 mL and Fourier-Transform Infrared (FTIR) Spectroscopy performed at an Agilent Technologies spectrometer, model Cary 630, with ATR accessory, Selenium, and Zinc crystals.

3. RESULTS AND DISCUSSION

3.1. Chemical Reduction via Sodium Citrate

The literature shows that the synthesis of gold nanoparticles by the chemical reduction method with Sodium Citrate can be confirmed through visual changes in the color of the solution. Initially, it turns yellow because of the presence of Au^{3+} ions to colorless in the presence of the reducing agent. During the chemical reaction, it changes to a very dark blue tone, changes to purple until it stabilizes in a reddish color, thus confirming the complete reduction of gold ions into metallic gold and the formation of gold nanoparticles (Figure 2) [7].

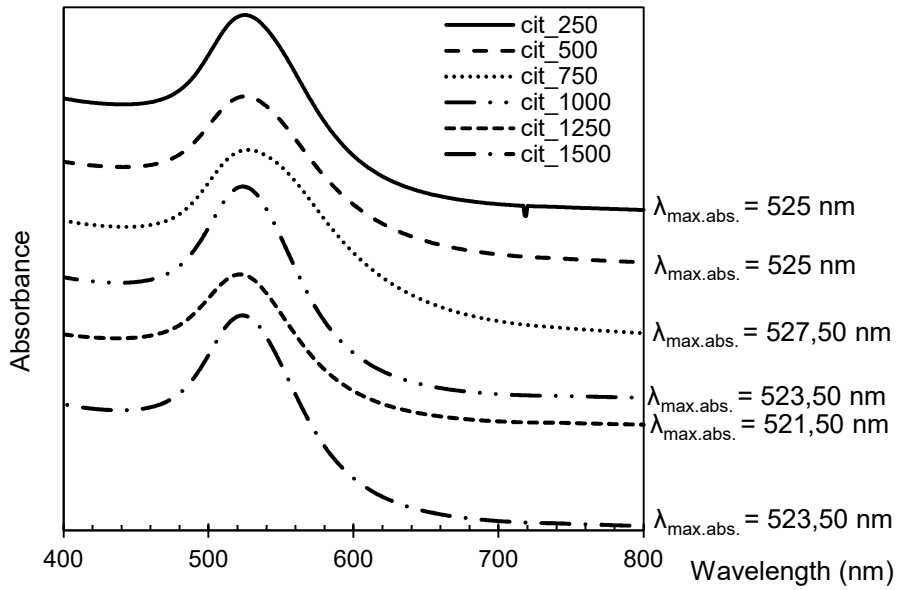
Figure 2. Gold colloidal solutions synthesized with Sodium Citrate



3.1.1 UV-vis Spectroscopy

Figure 3 shows the UV-visible spectra of AuNPs samples synthesized via chemical reduction with Sodium Citrate.

Figure 3. UV-visible spectra of Citrate-AuNPs



We can note that there is a maximum absorbance band between 500 and 550 nm in all spectra, indicating the presence of metallic gold and confirming the formation of gold nanoparticles [2]. Other studies also obtained spectra similar to Figure 3, with different maximum absorbance bands ($\lambda_{max.abs.}$), indicating distinct particle sizes (Ø), respectively: $\lambda_{max.abs.}$=519 nm and Ø≈9.0 nm [8], $\lambda_{max.abs.}$=520 – 524 nm and Ø≈10.0 nm [9], and $\lambda_{max.abs.}$=520 nm and Ø≈13.0 nm [10].

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3.1.2 ATR-FTIR Spectroscopy

All six spectra show similar behavior and the same absorption bands (Figure 4). The broad absorption band identified between 3,000 and 3,500 cm-1 indicates the presence of the hydroxyl functional group (-OH) in the solutions, resulting from the solvent used during the synthesis, which was ultrapure water. The peak at approximately 1636 cm-1 is characteristic of the double bond between carbon and oxygen, present in carboxylic acids, as β-Ketoglutaric acid, produced during the chemical reaction between Sodium Citrate and Chloroauric Acid (Figure 5).

Figure 4. ATR-FTIR spectra of Citrate-AuNPs

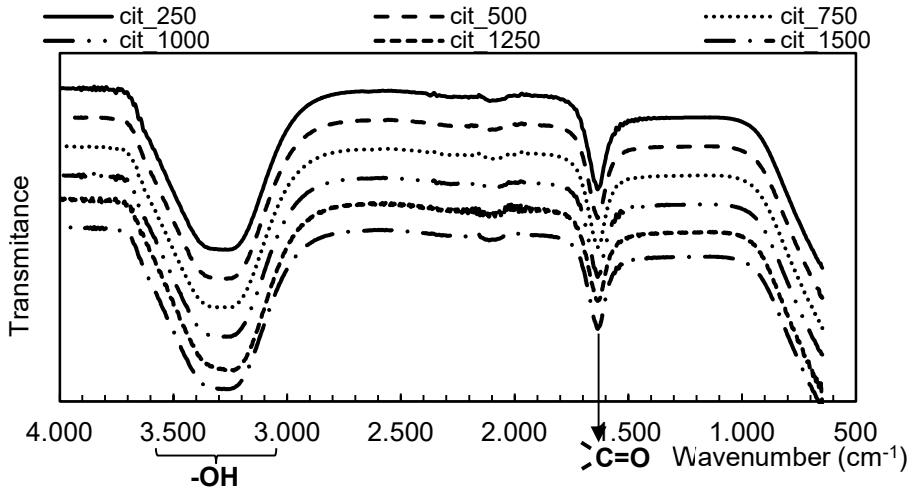
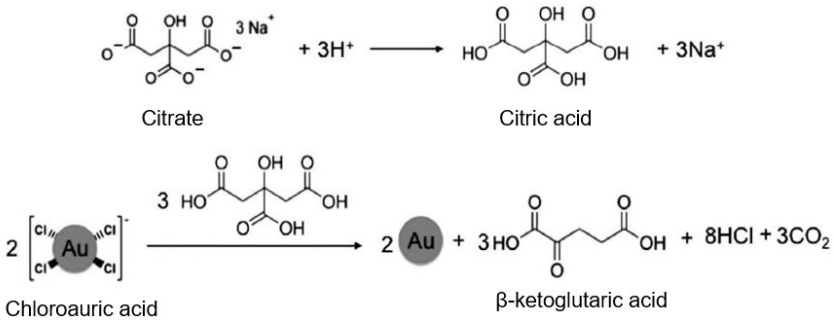


Figure 5. Reactions involved in the synthesis of Citrate-AuNPs [7]



3.2. Chemical Reduction via Sodium Borohydride

Figure 6 shows the photographs recorded during the synthesis of gold nanoparticles by the chemical reduction method with Sodium Borohydride, showing the visual changes in color solutions that occurred during the process.

Figure 6. Record of preliminary synthesis of AuNPs with Sodium Borohydride

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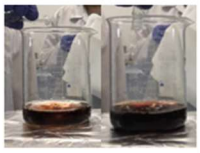
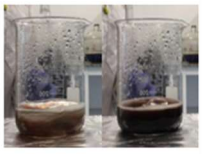
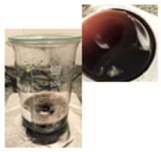
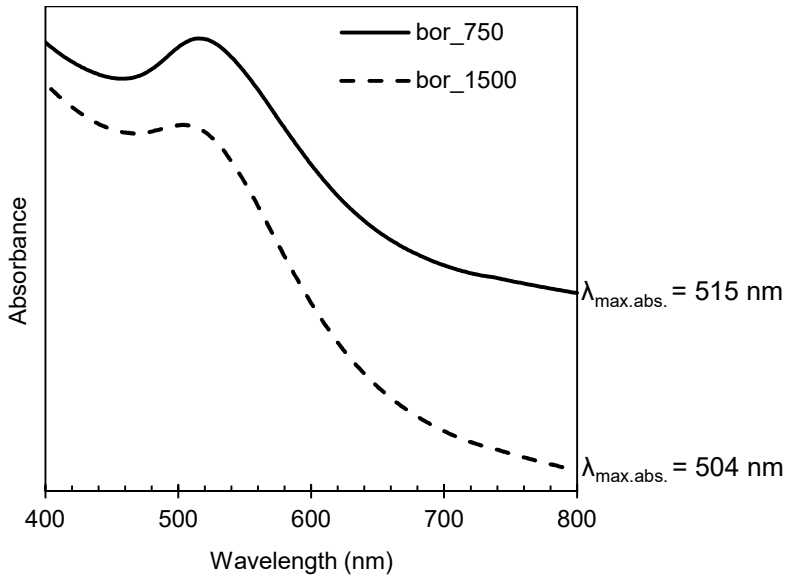
Sample	Chloroauric acid + Ultrapure water	Addition of stabilizer	Stirring Δt=30 min	Addition of reducing agent	Stirring Δt=1 h	Final solution
bor_750						
bor_1500						

We assumed that the chemical reduction of the Chloroauric Acid gold ions to metallic gold happened since, in both syntheses, an instantaneous change in the color of the solution to dark red with the addition of Sodium Borohydride was evidenced (Figure 6) [6]. After the reaction, the solutions maintained their dark appearance, whose red/brown color was identified by placing the samples against the light.

3.2.1 UV-vis Spectroscopy

Figure 7 shows the spectra in the UV-visible region of AuNPs samples synthesized via chemical reduction with Sodium Borohydride.

Figure 7. UV-visible spectra of Borohydride-AuNPs

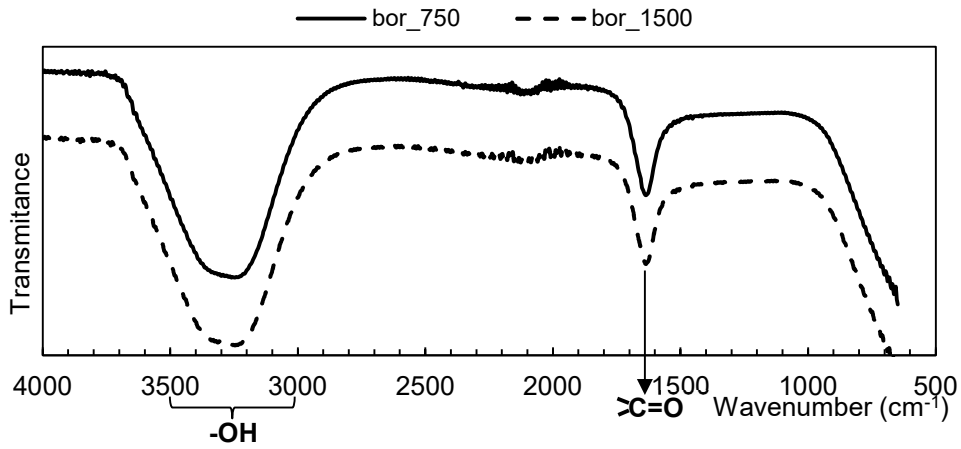


The spectra in Figure 7 show an absorption band between 500 and 550 nm, indicating the presence of metallic gold and confirming the formation of gold nanoparticles. However, unlike samples synthesized with Sodium Citrate, the plasmonic resonance band of gold in samples bor_750 and bor_1500 is less pronounced than in the others. The synthesis of gold nanoparticles with Sodium Borohydride as a reducing agent and a stabilizer used polyallylamine hydrochloride, 3-mercaptopropionic acid, and Polyvinylpyrrolidone was also observed by other authors [6,12].

3.2.2 ATR - FTIR Spectroscopy

The broad absorption band in Figure 8, between 3,000 and 3,500 cm^{-1} is characteristic of the hydroxyl functional group (-OH), resulting from the presence of ultrapure water in the medium. The band at 1,636 cm^{-1} consists of a superposition band because of the stretches of C=O and N-H groups combinations. The absence of absorption bands around 1,285 and 1,460 cm^{-1} suggests the breakage of the pyrrolidone ring during the reaction because of the C-N bond and the CH and CH_2 groups present in the chemical structure of the PVP [13].

Figure 8. ATR-FTIR spectra of Borohydride-AuNPs



3.3 Comparison between reducing agents

Table 1 presents a comparison between the reducing agents evaluated.

Table 1. Comparison between reducing agents

Feature	Sodium citrate	Sodium Borohydride
Particle size	4 - 100 nm [14]	1 - 30 nm [14]
Particle size distribution	Monodispersion [15]	Polydispersion [15]
Visual appearance	Red, purple, pink and orange [16]	Brownish color
Toxicity	Non-toxic reagent	It has acute toxicity
Function	Reducing and stabilizer reagent [7]	It requires the addition of stabilizing agents
Heating	Requires heating	No heating required
Time	Quick synthesis	Longer synthesis
Synthesis effectiveness	Identified by changing the solution's color (light yellow to red)	Identified in the UV-vis analysis

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4. CONCLUSION

The results showed colloidal solutions of gold nanoparticles produced with Sodium Citrate presented visual changes, which could be related to the efficiency of the synthesis, without the need to carry out the characterization. The characterization analyzes contributed to confirm the visual result obtained and showing the interference of the stirring speed with the characteristics of the synthesized nanoparticles. The confirmation of whether the synthesis of gold nanoparticles with Sodium Borohydride was possible only after UV-vis analysis since the solutions obtained showed brownish and dark colors. Absorbance bands and wavenumber results followed the current literature.

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