

COMPARATIVE STUDY OF GUM ARABIC AND PVP AS STABILIZING AGENTS FOR SYNTHESIS OF GOLD NANOPARTICLES

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ABSTRACT

Use Colloidal metallic nanoparticles such as gold nanoparticles have received a great attention, due in part to their specific properties and potential applications. Control of size and uniformity of nanoparticles is important to prevent aggregation. High-molecular-weight polymers were used as stabilizer agents. Natural polymers, such as gum Arabic, are used as stabilizer because of capping nanoparticles behavior and present advantages such as solubility, non-toxicity and its compatibility for pharmaceutical and biomedical applications.

Previous studies showed that the hydrophilic group of Poly(vinyl pyrrolidone) (PVP) caused repulsion on gold nanoparticles's surface because steric interactions with polymer, for this reason this kind of polymers could be used as stabilizer agent. The aim of this work is to study the synthesis and stabilization of gold nanoparticles with PVP and gum Arabic using gamma radiation. The results obtained by samples analysis using UV-Visible showed that the gamma irradiation doses influenced the nanoparticles formation by PVP but that is not the case with the GA, because for smaller quantity of Arabic gum in different doses produced and stabilized nanoparticles. The samples were observed for 20 days and showed stability. We have obtained preliminary results showed that the use of radiation is applicable to the formation of gold nanoparticles.

1. INTRODUCTION

Due to their unique physical, chemical, optical, electrical and catalytic properties, gold nanoparticles (AuNPs) have received considerable attention for potential applications in the fields of physics, chemistry, optics, biology, electronics and materials science as well properties for transporting and unloading the pharmaceuticals [1,2]. AuNPs are defined by tiny size, significant quantities of AuNPs are likely required in many commercial and industrial applications. Remarkably, novel emerging applications bring a huge growth of the global demand of AuNPs. For instance, biomolecule- and/or biopolymer-conjugated AuNPs are largely used as biomarkers and biodelivery vehicles in the medicine/pharmacy, and in cosmetic products, AuNPs are employed as anti-aging components for skin protection [3].

The use of ionizing radiation for the synthesis of metal nanoparticles is promising as highly reactive species with high reduction potential are produced in situ by the radiation, which is hard to achieve by other chemical methods. These reactive species can easily reduce metal ions down to zero valent state. Furthermore, because of its ability to fine-tune the radiation dose, dose rate and to selectively generate the required transient reactive radicals, it may offer better control over the size and the size distribution. Also it is a room temperature process

and the reaction system is cleaner since it requires no external chemical reducing agent. Irradiation of aqueous solution by high energy radiation generates transient radicals through water radiolysis. These transient radicals contain both reducing as well as oxidizing species. To create a total reducing condition specific solute is added, which can scavenge the oxidizing species. The reducing radicals such as e_{aq}^- and H^* are utilized to reduce metal ion precursor to metal in zero valent state. These metal atoms coalesce to form metal nanoparticles in presence of a capping agent [4].

Poly(N-vinyl-2- pyrrolidone) (PVP) has been used as drug carrier for various drugs in several reports [5], is one potential AuNPs stabilizing reagent due to its high solubility in many solvents, high stability and non-toxicity. PVP has been reported as a suitable capping agent in preparation of metal nanoparticles because it has functional groups and long polymer chain [4]. The hydrophilic headgroup (N–C=O) of PVP is attached to the surface of the particles, resulting in particle repulsion due to steric interactions between polymers adsorbed on the particle's surface [6].

Gum arabic (GA), a natural composite polysaccharide derived from exudates of *Acacia senegal* and *Acacia seyal* trees, is one of the most commonly used food hydrocolloids. GA serves as a very efficient emulsifier and a long-term stabilizer in food and cosmetic products containing oil–water interfaces. Much research has been conducted over the years to reveal the molecular structure of the gum and to relate it to its exceptional surface-active and rheological properties [7]. GA can be used as both a stabilizing and reducing agent. This property has been used to synthesize both nonradioactive and radioactive AuNPs with steric stability [8].

In our laboratory we have great interest in the study of the synthesis of gold nanoparticles. In this context, the aim of this study is investigate the effect of Arabic gum (GA) and Poly(N-vinyl-2- pyrrolidone) (PVP) as reducing and stabilizers agents in gold nanoparticles formulation using the gamma irradiation. In this paper, we reported our first results of the synthesis.

2. EXPERIMENTAL SECTION

2.1. Materials

Sodium tetrachloroaurate (III) dihydrate ($NaAuCl_4 \cdot 2H_2O$) (99,9%) from Sigma-Aldrich, Poly(N-vinyl- 2-pyrrolidone) (PVP) 90K from Êxodo, pure Gum Arabic from Synth; isopropyl alcohol (99,5%), prior to use, glassware was cleaned with aqua regia (volume ratio $HNO_3/HCl = 1:3$), HNO_3 (70%) and HCl (36,5%) from Sigma-Aldrich, and thoroughly rinsed with MilliQ water [9] and dried.

2.2. Gold nanoparticles synthesis

A stock solution of 1 mmol L^{-1} $NaAuCl_4$ was prepared by salt dissolution in MilliQ water. A stock solution of Arabic gum (1%) was prepared by dissolving the polymer in MilliQ water.

A stock solution of PVP (1%) was prepared by dissolving the polymer in MilliQ water and kept under heating at 100 °C during 40 minutes.

The GA solution was heated to 55 °C under stirring. The NaAuCl₄ solution was added under stirring and heating for 2 minutes.

The PVP solution was heated at 70 °C and the NaAuCl₄ solution was added under stirring and heating for 45 minutes

The gold nanoparticles synthesis with gamma radiation was prepared with addition of 2-propyl alcohol (50 µL). The samples were kept under refrigeration (4 °C) before and after irradiation. The γ -irradiation source of the laboratory is a ⁶⁰Co, and irradiated at dose rate of 5 kGy/h at 7.5 and 15 kGy in the Multipurpose Gamma Irradiation Facility at the Radiation Technology Center - IPEN.

The samples were prepared at a concentration and a range of doses as shown in Table 1.

Table 1: Samples preparation and doses applied.

NaAuCl ₄ (1mmol L ⁻¹)	GA (1%)	PVP (1%)	Dose (kGy)
7.0 mL	3.0 mL	-	-
7.0 mL	3.0 mL	-	7.5
7.0 mL	3.0 mL	-	15
0.5 mL	-	9.5 mL	-
0.5 mL	-	9.5 mL	7.5
0.5 mL	-	9.5 mL	15

2.3. Gold nanoparticles characterization

The AuNPs were characterized by UV–visible spectroscopy in the Spectrophotometer SpectraMax I3 to confirm the peak surface plasmon resonance of the AuNPs at $\lambda = 540$ nm, approximately. Solutions containing nanoparticles were analyzed and compared for 20 days.

3. RESULTS AND DISCUSSION

With heating and after irradiation, the initially colorless solution turns pink, its UV–visible spectra exhibiting an absorption band around 530 – 540 nm. This absorption is characteristic of the surface plasmon resonance phenomenon shown by gold nanoparticles [10].

When an aqueous solution containing Au⁰, PVP, GA, 2-propyl alcohol is subjected to gamma irradiation, the radiolysis of water occurs as a result of transient reactive species.

The 2-propyl alcohol present in there action medium reacts with H[•] and [•]OH to give 2-propyl radical reacts with e⁻_{aq} to give 2-propyl radical. The 2-propyl radicals are capable of reducing

Au^{III} . Hence the only reducing species present in the system is 2-propyl radical, which reduces the metal ion to metal in zero valent state (Au^{III} to Au^0) [4].

The Fig. 1 shows the formation of gold nanoparticles using heating and gamma radiation with GA as reducing agent and stabilizer (Au-GA). It was observed that heating is able to promote the reduction of gold salt to form nanoparticles, but the solution is less stable when compared with the nanoparticles formed by radiation after 20 days. The results of the samples using different radiation doses (7.5 kGy and 15 kGy) in solutions containing Arabic gum, not shown influence of the dose on the formation or stability of the AuNPs.

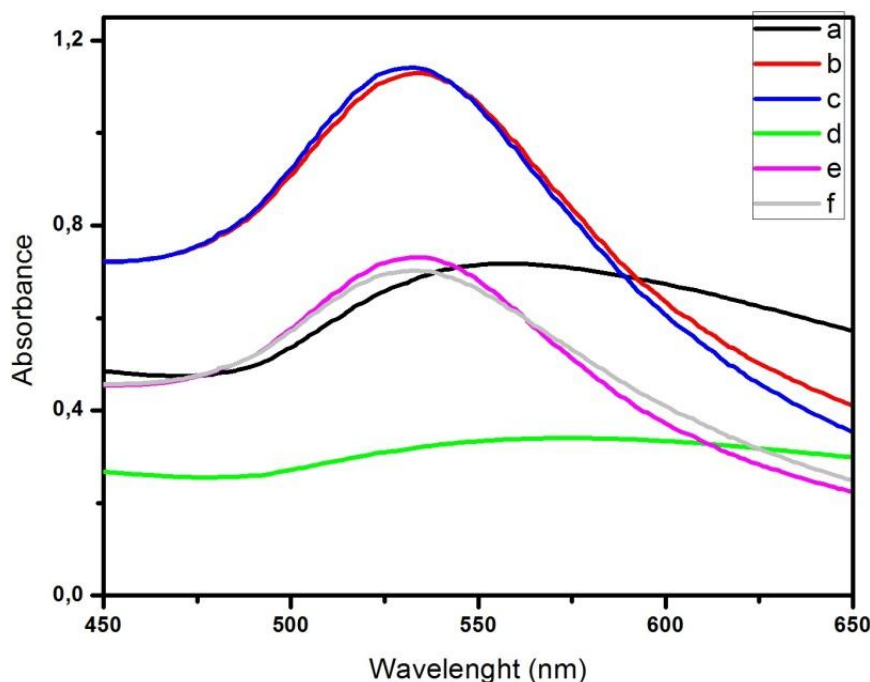


Figure 1: UV-Vis spectra of gold nanoparticles solution reduced by gum Arabic with different doses. (a) Au-GA non-irradiated, (b) Au-GA 7.5 kGy, (c) Au-GA 15 kGy, (d) Au-GA non-irradiated after 20 days, (e) Au-GA 7.5 kGy after 20 days, (f) Au-GA 15 kGy after 20 days.

After the heating was observed color change from clear to dark blue solution, but in the samples submitted to radiation was observed color change from clear to pink, both confirming the obtaining of nanoparticles.

The Fig. 2 shows the use of PVP as stabilizer and reducing agent and the results of the samples obtained by synthesis with heating and gamma radiation to form gold nanoparticles (Au-PVP). It was observed that nanoparticles formed by heating demonstrated less stability when compared with gold nanoparticles obtained by radiation. It was observed that lower doses of gamma radiation showed an increase in the formation of gold nanoparticles compared higher doses.

The analysis of the obtained curves it can be seen that the PVP was able to maintain stable gold nanoparticles for 20 days, with little change in their characteristics. The results of UV-

Vis absorption spectra in Fig. 1 and 2 show peaks around $\lambda_{\max} = 535\text{--}540\text{ nm}$, indicating the formation of AuNPs [11]. It was observed that after 20 days the gold nanoparticles obtained by PVP and irradiated showed stability with no significant difference from the previous period.

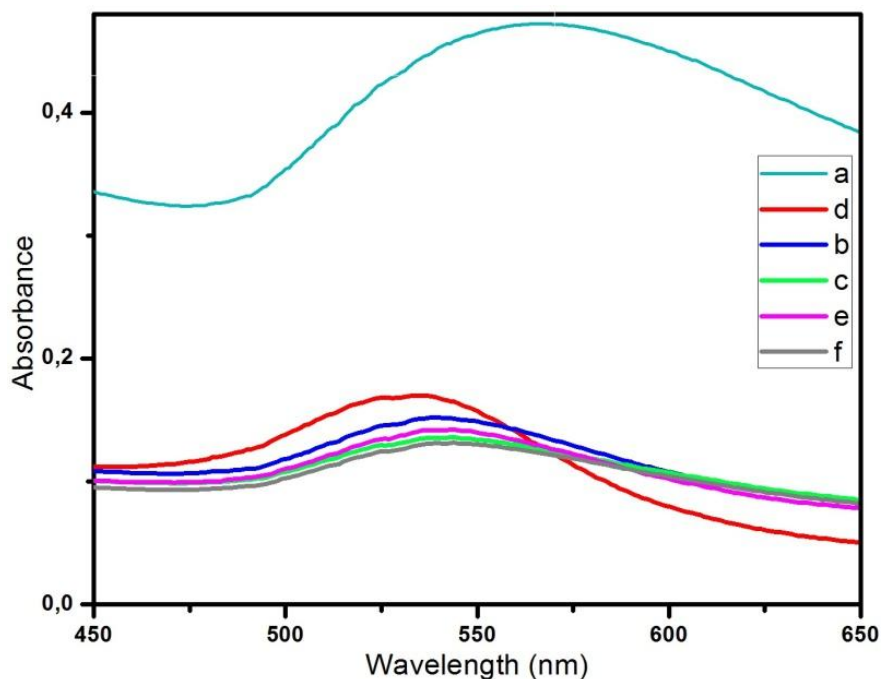


Figure 2: UV-Vis spectra of gold nanoparticles solution reduced by PVP with different doses. (a) Au-PVP non-irradiated, (b) Au-PVP 7.5 kGy, (c) Au-PVP 15 kGy, (d) Au-PVP non-irradiated after 20 days, (e) Au-PVP 7.5 kGy after 20 days, (f) Au-PVP 15 kGy after 20 days.

The results of the nanoparticles obtained with gum arabic and PVP showed that after 20 days the concentration of the nanoparticles decreases, which is observed by the decrease in absorbance peaks, but the nanoparticles are present, since the characteristic peaks at wavelength between 530-540 nanometers still prevail.

4. CONCLUSIONS

This paper reports our first results on the synthesis of gold nanoparticles using Arabic gum and PVP via γ -irradiation. The final color solution and the UV-Vis spectra with peak in 540 nm approximately, determined that the obtained nanoparticles.

The group concluded that the amount of gum arabic in relation to PVP may be less for the formation of gold nanoparticles using the synthesis by heating or radiation. The amount of nanoparticles obtained by radiation demonstrates that GA formed most AuNPs and curves with defined peaks when compared to the use of PVP.

These nanoparticles are stable in solutions of GA and PVP for at 20 days, when kept refrigerated indicating a simple process and economical method. There was no significant

difference from the irradiation doses used because the comparative results showed that 7.5 kGy and 15 kGy had little variation in UV-Visible.

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