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Assessment of long-term stability in silver nanoparticles generated by gamma radiation

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ABSTRACT

A modified electrolytic method that employed the suspension of silver ions (Ag^{+}) and subsequent exposure to gamma radiation at doses of 10, 25, 50, and 70 kGy (kGy) formed the silver nanoparticles (AgNPs). The stability of the AgNPs was monitored over a period of 12 months using UV Vis Spectrophotometry (UV–Vis), Transmission electron microscope (TEM) and Dynamic light scattering (DLS). In particular, AgNPs irradiated at 10 kGy exhibited the most favorable stability of the samples tested, with the additional advantage of requiring less energy for production due to the lower dose employed.

1. Introduction

Nanoparticles based on metals such as silver, gold, copper, iron, zinc, and platinum, among others, have been the subject of considerable attention in the field of medicine, as their importance has also been documented in the scientific literature over the centuries [1,2].

AgNPs are typically synthesized in aqueous media through a chemical reduction process involving the reduction of Ag^{+} ions, typically derived from a salt such as silver nitrate ($AgNO_3$). To regulate the growth and prevent the aggregation of particles, it is essential to utilize a stabilizing agent in the solution, such as anionic, cationic, or neutral surfactants or polymers. In general, a variety of reducing agents are employed, including sodium citrate, ascorbic acid, sodium borohydride, elemental hydrogen, carbonate, and copolymers. Some of these agents serve both the reducing and stabilizing roles in the synthesis process [3,4]. The composition and concentration of both reducing and stabilizing agents exert a considerable influence on the size distribution and morphology of nanoparticles, which in turn affects their functional properties and their stability [5,6].

While some studies address the stability of nanoparticles (NPs), there is a notable lack of systematic research in the literature that evaluates the long-term stability of silver nanoparticles (Ag NPs). Most available studies only indicate that these particles remain stable without precipitation for a relatively short duration of [7].

The objective of this study is to examine the preparation of AgNPs using a precursor solution comprising Ag^{+} and sodium carbonate, the last one may function as a stabilizing agent for AgNPs due to its capacity to form an electrostatic stabilization through the creation of an electric double layer on the AgNP surface. Following the aforementioned, the present study employed γ irradiation of Ag^{+} in an aqueous medium, resulting in the formation of Ag^{0} through a redox reaction. Furthermore, the stability of AgNPs formed by gamma radiation from a Co-60 source over time has been investigated, with variations in irradiation dose and the absence of additional stabilizing or catalytic agents. In light of these considerations, a green method for obtaining stable AgNPs is presented.

2. Methodology

2.1. Synthesis of the AgNPs

A 0.25 ppm of sodium carbonate was added to Ag bar in 2L of distilled water to obtain 44 ppm of Ag + by electrolysis process (ADP solucoes). Then 20 mL of the samples were subjected to irradiation process at 10, 25, 50 and 70 kGy at room temperature and rate of 1.8 kGy/h. Before irradiation, oxygen was removed. The samples were irradiated at the Cobalt-60 multipurpose irradiator at the IPEN-CNEN Radiation Technology Center. Samples were analyzed by UV–Vis, DLS and TEM by 1 month and 12 months after irradiation.

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3. Results

3.1. Spectrometry (UV–vis)

The effects of radiation dose were investigated using UV–Vis spectroscopy. Fig. 1 shows the absorption spectra of AgNPs obtained at different radiation doses after one and 12 months of storage. According to the spectra, all samples exhibited surface plasmon resonance (SPR) between 409 nm and 423 nm at both time points, corresponding to AgNPs [8] (Table S1). However, the absorbance varied across samples: the highest intensity was observed in the 10 kGy treatment, while the 50 kGy sample showed the lowest intensity. Additionally, after 12 months, the SPR in all samples shifted to slightly higher wavelengths, suggesting AgNP sizes changes over time (see supplementary material Fig. S1) [9,10] and 25 and 50 kGy samples decrease their intensity.The SPR positions across all samples suggest that the particle sizes are similar. For the 50 kGy sample, the spectra indicated aggregation from the start, which is corroborated by the gray color of the colloid (Fig. S2), indicating aggregated AgNPs [11]. In contrast, the AgNPs at 10 and 25 kGy displayed an orange color, corresponding to well-dispersed particles. The 70 kGy sample exhibited a dark brick-orange color, suggesting a higher concentration of AgNPs compared to the 10 and 25 kGy samples, yet still with good dispersion (Fig. S2).

This outcome is associated with the aggregation of AgNPs throughout storage [8,9], as illustrated in Fig. 1.

3.2. Dynamic light scattering (DLS)

Table 1 illustrates the variation in particle size of AgNPs as a function of ionizing radiation dose. Despite the identical composition of the precursor solution, the application of different doses of gamma irradiation resulted in the formation of different sizes of AgNPs.

The hydrodynamic diameter for the samples irradiated at 10 and 70 kGy during the first month of the study is just over 30 nm, which appears to be consistent with the particle size observed in the TEM analysis. In contrast, the samples irradiated at 25 and 50 kGy seem to have larger sizes compared to those found in TEM (Table 1), with this effect being more pronounced in the samples irradiated at 50 kGy, where the difference is tenfold. Although it is well known that the hydrodynamic radius does not literally represent the particle size, smaller sizes were expected. This effect may be caused by the small size of the particles and possible agglomeration, where a grayish color is already visible in the solution (Supplementary Information S2). After 12 months, the hydrodynamic radius appears to increase for the 10 and 70 kGy samples, but the PDI value also increases, suggesting that the radius remains essentially constant.

Table 1
Hydrodynamic Diameters (nm) values and mean diameter AgNPs' size as a function of radiation dose.

Dose (kGy)	Hydrodynamic Diameters (nm)				Mean Diameter (nm) TEM	
	1 month	PDI	12 months	PDI	1 month	12 months
10	39.1	28.1	70.2	30.5	36.59 ± 10.16	30.86 ± 8.0
25	52.1	24.8	30.2	31.1	28.08 ± 4.53	36.38 ± 10.9
50	120.2	25.5	–	–	13.48 ± 3.50	12.5 ± 3.90
70	37.6	28.8	60.6	50.4	32.25 ± 6.10	28.09 ± 8.0

3.3. Transmission electron Microscopy (TEM)

As illustrated in Fig. 2 the macrographs of irradiated samples at 1 and 12 months after exposition to gamma radiation, the size was measured by Image J1.54 D (supplementary information),

The particles shown in the micrographs for all samples generally exhibit an amorphous shape, mostly spherical, with some triangular and elongated forms. The particle sizes are nearly consistent across all samples, averaging around 30 nm, except for the 50 kGy sample, where the size is approximately half. Aggregates were not observed in the TEM images; however, changes in UV–Vis spectra, color, and sediment formation were evident after 12 months in the samples irradiated at 25 and 50 kGy.

4. Discussion

There is no discernible difference in size between the particles produced with a dose of 10 kGy and those produced with a dose of 70 kGy but the last one tends to agglomerate more. The formation of the AgNPs by gamma irradiation is possible during the irradiation process and depends on the dose, and that the aggregation of particles occurs indirectly at the same time due to the free radicals produced in the irradiation which are attenuated by carbonate present in the solution. The sodium carbonate in the reaction is in a low concentration, it could be

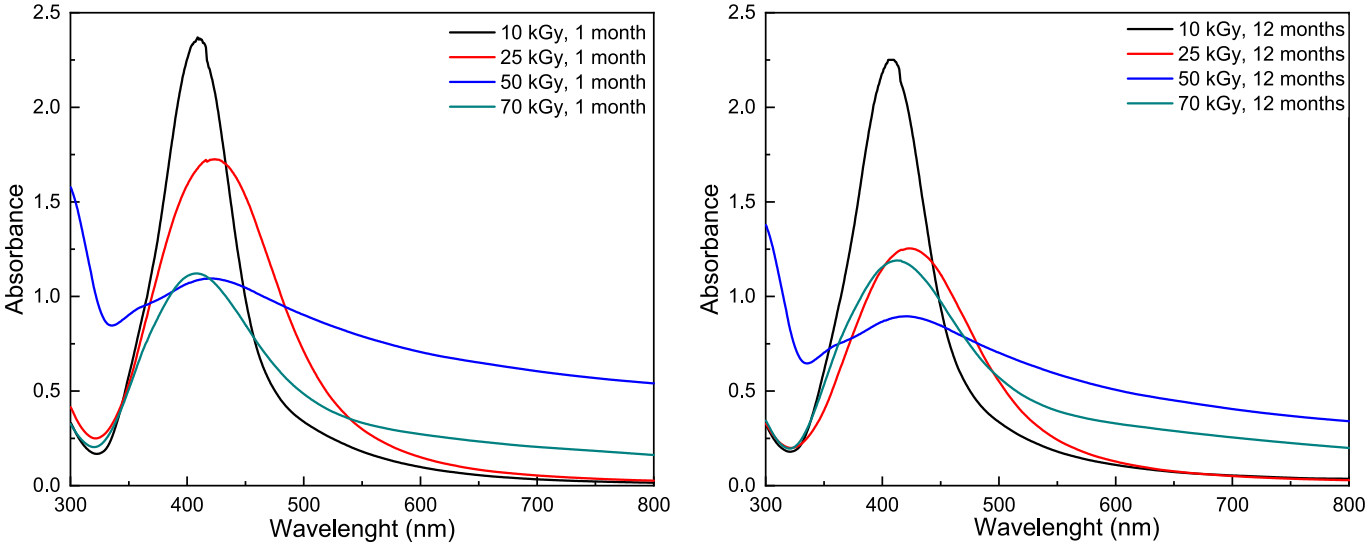

Fig. 1. UV–Vis spectra of the irradiated samples at 10 kGy, 25 kGy, 50 kGy, and 70 kGy doses, analyzed through a) one and b) 12 months.

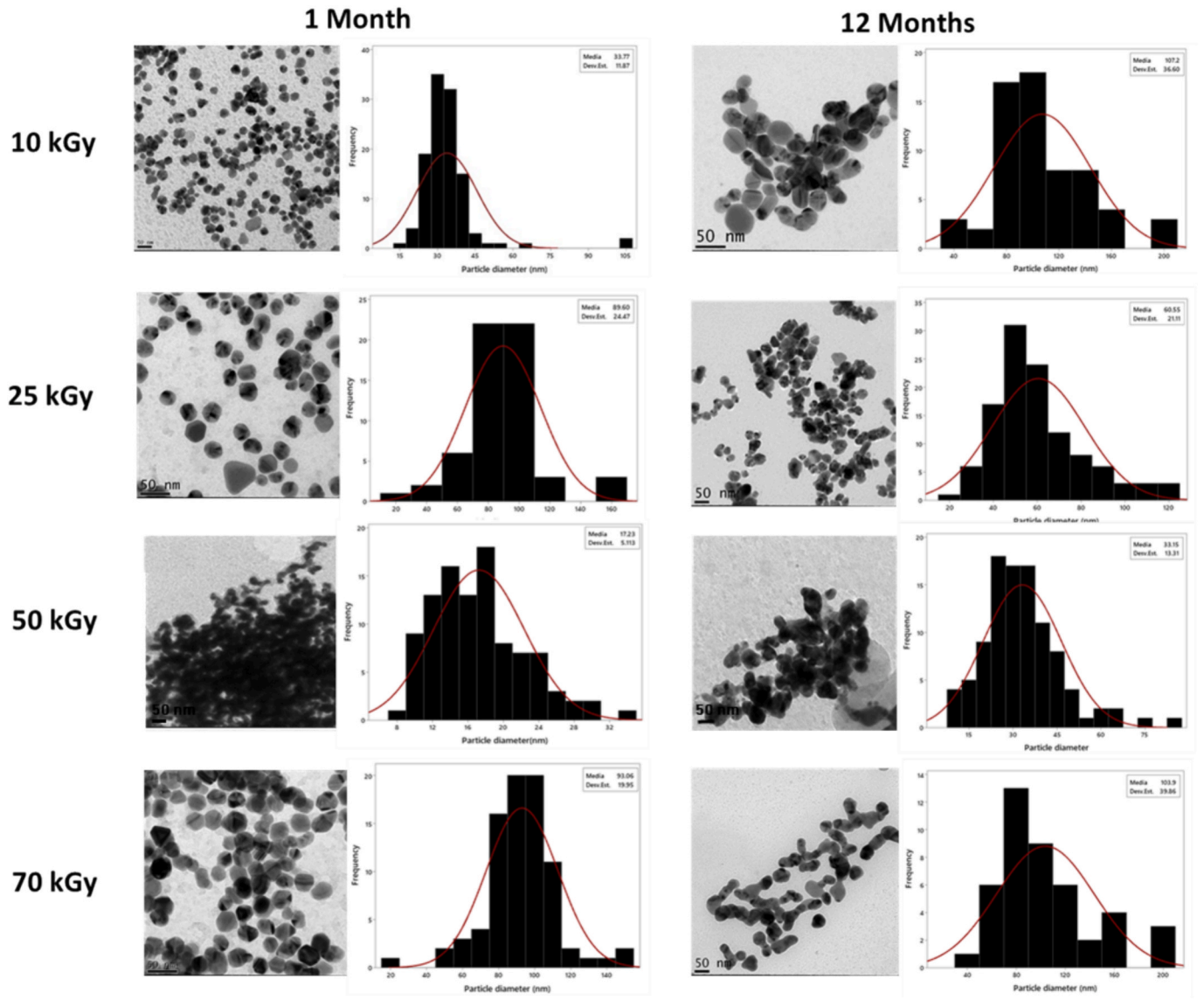

Fig. 2. Transmission electron micrographs of 10 kGy dose-sample, 25 kGy dose-sample, 50 kGy dose-sample, 70 kGy dose-sample.

consider this agent to act as radical scavenging, but, the samples have a different exposure time to gamma radiation, so the formation of AgNps and their stability is due to a synergy between the surface charge of AgNps and the radiation time (more information in Supplementary information).

The 10 kGy dose is the optimal choice for particle production when compared to the 25, 50, and 70 kGy doses according to UV–Vis and TEM experiments. This is because the 10 kGy dose facilitates the formation and dispersion of AgNPs, while the radiation energy is insufficient to produce the requisite number of free radicals for carbonate destruction, which is necessary to prevent AgNPs aggregation, consequently, a dose of 50 kGy is identified as the least optimal for preparing AgNPs.

5. Conclusion

The 10 kGy gamma irradiation dose is the optimal choice for the long-term production of well-dispersed AgNPs.

CRediT authorship contribution statement

Maria José Alves Oliveira: Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Gethzemani Mayeli Estrada Villegas:** Writing – review & editing, Supervision, Investigation, Conceptualization. **Larissa Otubo:** Writing – review & editing, Formal analysis, Conceptualization. **Abril Fonseca García:** Writing – review & editing, Visualization, Resources, Investigation, Conceptualization. **Giovanni Gonzalez-Pérez:** Writing – review & editing, Supervision. **Pablo Antonio Salvador Vasquez:** Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2024.137634.

Data availability

I have shared the data in Attach files step.

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