Synthesis of Ag nano-chitosan in lactic acid solvent by irradiation method

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Abstract. Colloidal Silver Nanoparticles were synthesized by Gamma ray irradiation in aqueous lactic acid solution containing chitosan as stabilizer. The aim of this research is to know the effect of irradiation dose and concentration of chitosan in the formation of Nano-silver. Silver Nitrate of 2 mM is dissolved in the chitosan solution. The effect of chitosan concentration which varied 0.3%, 0.5%, and 0.7%(b/v) were irradiated with gamma ray at dose of 5, 10 and 15 kGy. The formed of silver Nano were identified using UV–Vis spectrophotometer, particle size analyzer (PSA) and FTIR. The result shows, the concentration of chitosan (0.3 – 0.7%) in the irradiated solution also considerably affected the silver Nano particles size which decreased with increasing of irradiation dose. Due to the unique features of the processing procedures, thus γCo-60 ray irradiation has been considered as a suitable method for synthesis of colloidal silver nanoparticles.

1. Introduction
The application of Nano scale materials and Nano composites containing nanoparticles is an emerging area of Nano science and technology. Usually particles ranging from 1-100 nm in diameter are known as Nano particles [1, 2]. Being in Nano scale, these nanoparticles have high surface: volume ratio. Therefore, they often show unique and considerably different physical, chemical and biological properties compared to their macro scaled counterparts.

Generally, metal nanoparticles aggregate among themselves and progressively grow into larger clusters and eventually precipitates, deviating from Nano scale. This avoids the effectiveness of synthesized nanoparticles and discourages its application. Coalescence may be prevented by adding a cluster stabilizer. Synthetic polymers such as polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) are already in usage as stabilizing polymers of Ag Nano particle [2, 3]. Due to non-biodegradability and toxicity of synthetic polymers, at present a considerable attention has been drawn on the use of natural polymers to stabilize the Ag-Nano particle. Furthermore, especially in medical applications, additional steps are necessary to remove the synthetic polymer after synthesis, which makes the synthesis process much complex and less economic.

Therefore, Chitosan is a biodegradable, biocompatible and nontoxic polymer finds widely applications in food, pharmaceutical and fungicide, they are more favorable to be utilized as a stabilizer for synthesized of Ag-Nano particle. Chitosan shows unique polyatomic, chelating and film forming properties as it is an oxygen rich linear polysaccharide having active amino and hydroxyl groups [4]. Therefore, chitosan exhibits a number of interesting biological activities such as biocompatibility, biodegradability, non-toxicity, non-antigenicity and adsorption properties [4, 5].
Radiation has been recognized as a highly suitable tool for the formation of Ag-Nano particle and also radiation processing offers a number of advantages, such as easy process control, capability to combine Ag-Nano particle and sterilization in one step, no needs for initiators or cross-linkers, which may be harmful and difficult to remove [1,6]. These qualities make irradiation the method of choice in the development of a green method to synthesize Ag-Nano particle is desired method by using gamma radiation provides more convenient and a cleaner approach.

2. Experimental

2.1. Materials
Analytical grade silver nitrate and lactic acid as a solvent were obtained from E Merck. Chitosan can be obtained from chitin extracted from prawn shell (Penaeus monodon), it was got from Muara Karang, North Jakarta

2.2. Preparation of Ag+ solution and γ-ray irradiation
2.0 mM of Silver Nitrate was dissolved in the solutions containing chitosan with different concentration of 0.3%, 0.5% and 0.7% (w/v) were placed in glass tubes, and DE aerated by bubbling with nitrogen. The γ-ray irradiation was carried out in a Co-60 source with dose rate of 5.2 kGy/h at Pasar Jumat, Center for Research and Development of Isotopes and Radiation Technology, Jakarta, Indonesia.

2.3. Characterization
Optical spectra of the irradiated Ag+ solution which was diluted with water to 0.1mM calculated as Ag+ concentration were taken on an UV-Vis spectrophotometer model UV-2401-PC, Shimadzu, Japan. The size of the silver nanoparticles was measured using a particle size analyzer (PSA) Delsa Max and Infrared spectra were taken from a Fourier Transform Infrared Spectrometer (FTIR) (Bruker Tensor).

3. Results and discussion

3.1. Color
The color of each sample after irradiation was checked with naked eye to examine the formation of Ag-Nano chitosan is shown in figure 1. Ag Nano- chitosan which irradiated by gamma rays have been a change colors become pale yellow, a discoloration of solution is caused by the reduction of Ag+ to Ag0. The reactions mechanism are H2O \rightarrow e_{aq}, H+, OH-, H2O2, H2, H3O+, Ag+ + e_{aq} \rightarrow Ag0 and Ag+ + H+ \rightarrow Ag0 + H+.

![Figure 1](image)

Figure 1. Sample image before irradiated (A) and after irradiated at doses of 5 kGy (B), 10 kGy (C) and 15 kGy (D).

3.2 UV-visible spectroscopic
Each sample was analyzed by UV-visible spectrophotometer in the range 200-750 nm and the wavelength corresponding to maximum absorption was recorded. 0.3% (w/v), 0.5% (w/v) and 0.7% (w/v) chitosan in 1% (v/v) lactic acid solutions irradiated at dose of 5 kGy, 10 kGy, 15 kGy and the 0 kGy was used as control samples.

3.2.1. The uv–visible spectrum before irradiation (0 kGy). The spectrum was shown in figure 2. It can be seen that on the spectrum of a sample before irradiation of gamma ray (0 kGy), at concentrations Chitosan of 0.3% (b/v) shows the wavelength at 265 nm, concentration of chitosan 0.5% (b/v) is 269 nm, and the concentration of Chitosan 0.7% (b/v) generate wavelength 271 nm. The results prove that without irradiation does not generate the formation of silver Nano particles, where the silver nanoparticle formation occurs at a wavelength between 400 nm to 450 nm [7,8].

![Figure 2](image1.png)

**Figure 2.** UV-Vis Spectrum of solution without irradiation.

3.2.2. UV-visible spectroscopic of irradiated samples. Wavelength band of the UV-visible spectrum at 400-450 nm is indicates the formation of silver Nano particles. Figure 3 shows the samples irradiated at doses of 5kGy, 10 kGy and 15 kGy gave the characteristic peak wavelength band at 402 nm to 409 nm are indicating the formation of silver Nano particles.

![Figure 3](image2.png)

**Figure 3.** UV-Vis Spectrum of solution irradiated dose of 5 kGy, 10 kGy and 15 kGy.

From the figure 3, it can be seen that the spectrum of solution with difference concentration of chitosan after irradiated 5 kGy, 10 kGy and 15 kGy. The figure shows that a good synthesis of Ag Nano particles was achieved in 2 mM AgNO3 in 0.7% (w/v) chitosan solution. High chitosan concentrations promote the more stable than lower concentrations. When AgNO3 is mixed with chitosan before irradiation, Ag+ interacts with the electron abundant oxygen atoms of hydroxyl groups of the polysaccharide [9]. Generally the shape of the wavelength band is broad by increasing of concentration of chitosan because the nanoparticles lay in close proximity in their size, thus the gap between conductance and non-conductance bands of nanoparticles changes slightly. Therefore, each set of
particles having the same size, has its corresponding excitation due to both UV and visible radiation, thus broadening the wavelength band [9].

When there are a large number of polymer chains the number of functional groups and sites for Ag+ interaction increase. Then, there are more binding sites on the polymer as nucleation sites for the resulting Ag⁰ atoms to aggregate during the reduction of Ag⁺. Therefore, high polymer concentration promotes more binding sites. Also, high concentration of polymer acts as a physical barrier to avoid uncontrolled aggregation of Ag-Nano particles as there are more chains to envelope the surface of Ag-Nano particles [10].

3.3. Particle size distribution

Particle size showed a wide distribution. The size ranges from 30–250 nm in diameter, but only the particles ranging from 1-100 nm in diameter are considered as nanoparticles. Therefore, this sample contains particles which are in the nano range. Particle size distribution and the size of silver particle without irradiation show in figure 4 and table 1.

![Figure 4. The spectrum of particle size analyzer without irradiation.](image)

| Concentration of Chitosan (% w/v) | Particle size (nm) |
|----------------------------------|--------------------|
| 0.3                              | 250                |
| 0.5                              | 232                |
| 0.7                              | 204                |

From table 1 we can see that without irradiation at concentration of chitosan 0,3 %, 05 % and 0,7% the particle size of Silver are 250 nm, 232 nm and 204, respectively. From the above data it can be concluded that the samples without irradiation the Ag-Nanoparticles does not occurs, because the particle size measured is higher than 100 nm.

Figure 5 and table 2 shows the spectrum of Particle size distribution and particle size of Ag after irradiated at dose of 5 kGy, 10 kGy and 15 kGy.
Figure 5. The spectrum of particle size analyzer irradiated at dose of 5, 10 and 15 kGy

From figure 5 we can see that the spectrum of particle size analyzer of Ag-chitosan when irradiated a dose of 5 kGy, 10 kGy and 15 kGy. The figure shows that the particle size has a narrow distribution means that in each sample the size of the particles contained therein are of the same size. The particle size of irradiated Ag-particles it shown in table 2.

| Irradiation Dose (kGy) | Concentration of Chitosan (%w/v) | Particle size (nm) |
|------------------------|---------------------------------|-------------------|
| 5                      | 0.3                             | 98                |
|                        | 0.5                             | 96                |
|                        | 0.7                             | 84                |
|                        | 0.3                             | 83                |
| 10                     | 0.5                             | 77                |
|                        | 0.7                             | 73                |
|                        | 0.3                             | 56                |
| 15                     | 0.5                             | 43                |
|                        | 0.7                             | 30                |

From the table it can be seen that the particle size of Silver measured by particle size analyzer is from 30 nm to 100 nm. The particle size is less than 100 nm. so that the formation of Ag-Nano has been proven

3.4. FT-IR spectroscopic analysis

Figure 6 shows both in the sample before and after irradiation, although there is a possibility of overlapping N-H and O-H stretching vibrations, the strong band at 3000-3750 cm$^{-1}$ is characteristics of O-H stretching vibration [11]. In the wave number 1520-1680 cm$^{-1}$ there is a C = O group which is a carbonyl group derived from lactic acid and chitosan with 83% DD, so the remaining 17% is an acetyl group. In the wave number 1000-1260 there is a C-O- group of chitosan.

This suggests that the formation of Ag-Nano was promoted by O-H bond [12]. Authors believe that the electrostatic interaction of Ag-Nano to the O-H bond reduces the electron density which is distributed between O and H, decreasing the O-H bond strength. Therefore, the bond will now resonate at a lower frequency.
4. Conclusion
Based on the results of this research it can be concluded that Ag-Nano particle was successfully synthesized by irradiation technique. The irradiation dose of greatly influences in the formation of Ag-Nano particle, the higher of irradiation dose, and the smaller size of Ag-Nano obtained. The concentration of Chitosan as a stabilizer greatly affects the size of nanoparticles. The higher the concentration of Chitosan the size of nanoparticle is getting smaller. The optimal condition was the concentration of chitosan 0.7% and irradiation dose was 15 kGy the obtained of Ag-Nano particle is 30 nm.

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