Synthesis of silver nanoparticles from electronic scrap by chemical reduction

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Abstract
In the present research, the use of electronic waste in the synthesis of silver nanoparticles was investigated. For this purpose, electronic scraps were used as a consumable part to synthesize silver nanoparticles. The results revealed that by optimizing the time and temperature of the dissolution process using nitric acid solution up to 90%, silver can be extracted from these parts. The results indicated that the concentration of initial silver nitrate had a significant impact on the quality of the final product, so that the best conditions for the synthesis of silver nanoparticles with suitable properties were provided at 1 molar concentration. Phase studies indicated that the main phase of the synthesized silver particles had an FCC structure and no unwanted phase was observed. Ultraviolet–visible analysis of the synthesized powder revealed that the main peak for the silver nanoparticles appeared in the wavelength range of 400 to 450 nm. DLS analysis revealed that precursor’s particles inside the sol were below 15 nm. Based on AFM and TEM investigations, the particles synthesized under these conditions had nanometric spherical morphology with uniform particle size distribution.

Introduction
Recently, recovery and synthesis of electronic waste have become one of the most important issues for public sector managers as well as private sector investors. The public sector managers’ view on this issue is to take appropriate management measures to protect the environment and prevent contamination by the elements and metals in these compounds. Furthermore, private sector investors regard this as an opportunity to recover and extract these precious metals and elements as very cheap raw materials. Printed circuit boards (PCBs) account for one of the most important categories of electronic components and waste. Because of their valuable elements, the recovery and extraction of precious metals like silver will be among the new ideas in this regard. Typically, there is almost 0.1% silver metal available in an electronic circuit. Due to its high cost and the low cost of raw materials as well as the production of an advanced product (Nano-silver colloidal solution), the recovery and extraction of silver will make the present design one of the important projects in the academic research field in terms of innovation and justification. Owing to their unique properties, metal nanoparticles have special applications in various industries. These include specific electrical, magnetic, catalytic and optical properties. These properties provide certain applications in medical, biological, chemical, optical and electronic engineering [1–6]. Among the metal nanoparticles, silver nanoparticles play a crucial role due to their catalytic and antimicrobial properties [7, 8]. Nano-silver is a remarkable scientific achievement in nanotechnology that has applications in medicine and various industries, such as agriculture, animal husbandry, packaging, home appliances, cosmetics, health, and military. Different methods are used to synthesize silver nanoparticles. These include the chemical reduction of silver ions in aqueous or non-aqueous solutions, substrate-based methods, electrochemical reduction, ultrasonic resonance, photocatalytic or light emission reduction, microwave synthesis, radiation reduction, micro emulsion method, biochemical reduction, and sol-gel [9–11]. The most important issue in the synthesis of silver nanoparticles is to prevent them from agglomeration and adhesion during synthesis and storage [12, 13]. Certain organic substances, such as surfactants, polymers, and stabilizing
ligands, are commonly used to make the particles passive and prevent their aggregation. Organic compounds can prevent the adhesion of nanoparticles and allow them to be produced separately. Polymeric materials are also commonly used as protective agents to prevent agglomeration through their interaction with small nanoparticles. Selection of protective agents is one of the essential factors in the preparation of nanoparticles. Since nano-silver growth processes can be controlled through stabilizers, it is possible to manipulate the shape and size of silver nanoparticles by selecting different stabilizers. Therefore, different protective agents are available to obtain different forms of silver nanoparticles for target application. The most common synthesis method of silver nanoparticles is the chemical reduction of silver salts reducing agents, such as NaBH₄, citrate, and ascorbate. The use of highly potent reductants like borohydride will produce fine silver particles, but will make it difficult to control the growth of large particles [14–18]. Sondi et al used ascorbic acid as a silver reducing agent in silver nitrate solution [19]. In this method, silver hydrocele was obtained by adding 10 cm³ of 1 M ascorbic acid at a rate of 3 cm³ min⁻¹ to 90 cm³ of solution containing 5 wt.%. The silver salt solution obtained by using surfactants and reducing agents like meta-sulfides is converted to silver clusters in the liquid phase. At this point, the temperature, time and ratio of the reactants will be regarded as the process parameters and variables to produce a colloidal solution with a significant concentration (100 to 2000 ppm).

**Experimental procedures**

Materials used in this study include Ethanol solution (Ethyl Alcohol, (C₂H₅OH), Sigma Aldrich), electronic waste components, Nitric Acid, ((HNO₃), Sigma Aldrich), Liquids Containing Silver Salts, ((POZ/AgNO₃/BMIM⁺), Merck), Polyvinylpyrrolidone (PVP) with HAS-7% is a viscous solution, ((C₆H₉NO), Nippon Shokubai Company). Figure 1 represented the schematic for the synthesis of silver nanoparticles in this work.

To supply the required silver source, 10 g of electronic waste components were crushed from the center of the crystalagate mortar. A homogeneous powder was achieved and kept at 500 °C into an oven for 10 min to remove any possible contamination like grease. In the next step, the nitric acid solution was added to dissolve the silver content from the powder. Then, the liquid containing silver salt was separated by centrifugation at 6,000 rpm. Finally, the silver nitrate powder was obtained after drying for 24 h at 60 °C under a 10-millibar vacuum. To synthesize silver nanoparticles, first 5 grams of silver nitrate was first added to 100 ml of ethanol and stirred for 30 min. Next, the PVP solution (5% wt.) was added slowly and drops wise to the system, with 1 drop being added every 10 s. Finally, the system was mixed at a specific temperature and time. To investigate the effect of dissolution time on the final product characteristics, synthesis was performed at 30, 60, 90 and 120 min. In terms of the reaction temperature, the samples were synthesized at different temperatures of 20, 30, 40 and 60 °C. In addition, to investigate the effect of silver nitrate concentration on the quality of the finished product; samples were synthesized using 1 and 2 M silver nitrate solution in 100 cc of ethanol. Concentration of silver in

![Figure 1. Operational schematic for the synthesis of silver nanoparticles in this project.](image-url)
the solution was determined using wet chemistry analysis (ICP-OES) and atomic absorption spectroscopy. The samples were placed in sealed containers and then sent to Kansaran Binaloud Laboratory for the silver content analysis. A PerkinElmer Lambda 25 UV/Vis spectrometer was used to produce UV/visible spectra. For this purpose, the samples were poured into quartz containers of the apparatus, and spectroscopy was performed on samples in the range of 200 to 900 nm with an accuracy of 0.5 nm. The samples were also diluted to a ratio of 1:3 with pure ethanol to avoid device error due to masking and overcrowding. The synthesized samples were imaged using a Phillips CM200 transmission electron microscope at a working voltage of 100 kV. DLS method was used to determine the average particle size. An X’pert apparatus was used to prepare the diffraction pattern of samples with a copper (Kα) cathode lamp. The samples were placed on a holder after drying, and X-ray patterns were prepared at a rate of 1° min⁻¹ and diffraction angle range of 20 to 90. The analysis was performed using the AFM equipment manufactured by Veeco USA. The samples were first diluted with pure ethanol to a ratio of 1:5, and then one drop was poured onto a mica substrate, and the solvent was allowed to leave the system for 1 h.

Results and discussion

In the first step, the silver extraction rate was investigated at different temperatures for 30 min using a nitric acid solution. Figure 2 presents the extraction rates at different temperatures. As figure 2 shows, the extraction rate exponentially surged as the temperature increased from 25 to 80 °C. The silver extraction rate reached 75% at 80 °C. The extraction rate was calculated by equation (1).

![Figure 2. Silver extraction rate at different temperatures using nitric acid solvent for 30 min.](image)

![Figure 3. Silver extraction rates at 60 °C and in different dissolution times.](image)
Extraction rate = \( \frac{C_0 - Ct}{C_0} \times 100 \)  

(1)

Where \( C_0 \) is equal to 5000 ppm and \( C_t \) is the amount of silver in the nitric acid solution determined by the wet chemical analysis method.

According to equation (1), by increasing the amount of dissolved silver in nitric acid, the silver extraction rate increases. Therefore, by increasing the dissolution temperature, the silver extraction rate increased. Although, by increasing the temperature, the extraction rate increased, the optimum temperature was set to 60 °C due to the limitations and risks of increasing the nitric acid temperature. In addition, the amount of silver extraction rate differences at 60 °C and above was imperceptible. Figure 3 displays the dissolution time and the silver extraction rate.

As figure 3 reveals, by increasing the dissolution time from 30 to 60 min, the silver extraction rate was significantly increased, reaching approximately 92% over 60 min. However, by increasing the dissolution time from 60 to 90 min, all the silver content in the electronic waste was completely extracted to the nitric acid solution. These results indicated that it could take 1.5 h to dissolve all the silver content in the electronic waste using 1 M nitric acid at a process temperature of 60 °C. However, to reduce the energy and costs, the processing time could be set to 1 h. In this way, only 8% of the silver in the electronic waste would not be extracted which was acceptable. Thus, by considering economic terms, the optimum extraction process time would be set to 60 min. The reaction time for silver ion reduction in the presence of ethanol was an important process parameter that must be carefully investigated in all silver nanoparticle synthesis systems. As mentioned earlier, to synthesize silver nanoparticles, samples were prepared in three different periods to carefully examine the effect of these parameters on the quality of the final product. It should be noted that in the preparation of these samples, the concentrations of silver nitrate and polymer were set to 1 M and 0.5 M, respectively. As the particle size was the most important required parameter, ultraviolet spectroscopy was used to investigate the effect of different process periods on the nanosilver particle size. Figure 4 depicts the effect of the process time on the final materials’ properties measured by the UV spectrum. As figure 4 shows, increasing the time from 30 to 60 min
Figure 6. DLS particle size and distribution of silver nanoparticles at different concentrations of silver nitrate: (a) 1 M and (b) 2 M.

Figure 7. X-ray diffraction pattern of silver nanoparticles with a concentration of 1 M in the diffraction angle range of 20 °C–80 °C.
has shifted the position of the main peak ($\lambda_{\text{max}}$) to higher wavelengths, and the intensity has slightly increased. However, in the sample prepared for 90 min, the changes were not noticeable compared to the 60 min prepared sample. Despite a very slight increase in $\lambda_{\text{max}}$, the sample characteristics were not noticeably changed from 60 to 90 min. This result indicates that by increasing the reaction time from 30 to 90 min, the nanoparticle size increases due to the growth and bondings of primary clusters. This particle growth was quite noticeable up to 60 min. The significant decrease of the Ag$^{+}$ concentration was the main reason. In other words, silver ions were required to increase the final particle size and the growth of the clusters [20].

Figure 5 presents the UV/Visible spectrum of the sample synthesized at 60 °C for 1 h. As the figure shows, the main peak was observed in the range of 400 to 450 nm, which was attributed to the main peak of the silver nanoparticles. The presence of the main peak with the maximum intensity in this position was exactly consistent with the results.

The mechanism of the silver nanoparticle synthesis and the transformation of Ag$^{+}$ to Ag was one of the most important factors that must be carefully investigated in all silver nanoparticle synthesis processes. Ethanol had a reductive role in the system. It could be oxidized and converted to secondary alcohols. To illustrate the ethanol reductive role, it could be oxidized to aldehyde or ketone depending on system conditions, which occurs more rapidly in the presence of metal ions. Temperature also plays an important role in the ethanol oxidation reaction; therefore, at higher temperatures, more Ag$^{+}$ is recovered by ethanol per unit time, resulting in the formation of
high Ag nuclei per unit time and reduced size of synthesized nano silver particles. The population of these particles also increases significantly, all of which can be deduced from the results of the presented spectra.

Figures 6(a) and (b) show the particle size and distribution in the solutions with the concentrations of 1 M and 2 M, respectively. By comparing the DLS curves for these two samples, the sample with the 2 M concentration of silver nitrate had a wider particle size distribution. The silver nanoparticles had a size in the range of 8 to 30 nm. However, in the sample with the 1 M concentration of silver nitrate, the DLS curve indicated a narrow particle size range, with a lower average particle size of approximately 15 nm. Therefore, it could be concluded that the sample containing 1 M silver nitrate had an ideal concentration for the final product particle size and distribution. Figure 7 shows x-ray diffraction pattern of silver nanoparticles with a concentration of 1 M in the diffraction angle range of 20 °C–80 °C.

Based on the XRD result, the synthesized silver nanoparticles had a crystalline structure. Therefore, several peaks corresponding to the silver crystal planes were observed in this pattern. The peaks appeared at angles of 38.15, 44.4, 65, and 78 degrees. These peaks were attributed to the main planes of silver with cubic phase (FCC), including (111), (200), (220), and (311). There were not any extra peaks in the pattern, on firming the high purity of the synthesized nanoparticles. The lattice index \( a_0 \) was approximately 4.08 Å calculated from x-ray diffraction patterns, which perfectly matched the silver lattice index of 4.086 Å reported in the references (JCPDS No. 0783-04). According to the Shearer equation, the crystallite size was calculated at approximately 105 Å. AFM was used to scrutinize the morphology and size of the synthesized silver nanoparticles (figure 8). As figure 8 shows, the atomic force microscopy image of these nanoparticles clearly indicates the uniform particle size and distribution of synthesized nanoparticles. The average particle size was estimated at 15 nm, which was already shown by the DLS results.

The morphology and uniformity of the synthesized silver nanoparticles were studied by electron microscopy. Figure 9 displays the transmission electron microscopy images of silver nanoparticles with a concentration of 1 M. According to figure 9a, the average particle size was in the range of 10 nm to 15 nm and had a uniform distribution with spherical morphology. The TEM images are consistent with the DLS analysis results.

**Conclusion**

In this project, the synthesis of silver nanoparticles was investigated by chemical reduction using ethanol as a solvent and a reducing agent. One of the main goals of this work was the use of electronic component waste as a primary silver source. There were some prominent results in the present project as follows:

1. The used electronic components so-called ‘electronic wastes’ are one of the most important sources for the extraction of valuable metals, such as rare earth metals, gold, and silver. Crystal oscillators are a rich source of silver, particularly their inner parts.

2. The use of nitric acid at a certain concentration and the temperature of 60 °C for 1 to 2 h provided the best conditions for silver extraction with an efficiency of 95%.

3. Silver nanoparticles were synthesized using a silver nitrate solution obtained from electronic waste by the PVP capping method and ethanol as a solvent and a reducing agent. The results indicated that silver nanoparticles with optimum properties were successfully synthesized at an initial silver nitrate concentration of 1 M to 2 M and an appropriate ethanol molar ratio.

4. According to the UV/Visible spectroscopy result, if the initial nitrate concentration is equal to 1 M, the process time does not significantly affect the number of synthesized nanoparticles and the particle size. However, the process temperature had a strong effect on the particle size. By changing the process temperature, the particle size changed from 10 nm to over 300 nm.

5. The DLS analysis results showed that as the concentration of silver nitrate increased from 1 M to 2 M, the final particle size increased, and the particle size distribution changed from narrow to a wider distribution and lower quality. Therefore, the concentration of 1 M of silver nitrate was used to obtain an optimum final powder.

6. X-ray spectroscopy of the sample prepared at 1 M concentration exhibited pure silver peaks and a cubic crystalline structure (FCC) for the synthesized powder. The crystallite size was calculated to be approximately 105 Å based on the Shearer equation.

7. Transmission electron microscopy images also revealed that the use of a 1 M silver nitrate solution to synthesize nano silver increased the quality of the final particle. Hence, the particle size was 15 nm with uniform spherical morphology.
Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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