



SYNTHESIS OF SILVER NANOPARTICLES (AGNPS) FROM SILVER CONTAINED WASTES, A REVIEW

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Abstract

Silver nanoparticles (AgNPs) have garnered significant attention for their antimicrobial properties and their diverse applications across industries such as healthcare, pharmaceuticals, food, and cosmetics. This review highlights the synthesis of AgNPs from silver-containing waste materials, exploring the various methods, including physical, chemical, and biological techniques. Among these, biogenic methods are preferred due to their simplicity, cost-effectiveness, and environmental friendliness. The review covers the potential sources of silver in waste materials such as electronic waste, photographic films, and industrial byproducts, and discusses the processes for extracting silver and converting it into nanoparticles. Additionally, the study examines the use of plant extracts and other biological agents for synthesizing AgNPs, emphasizing the importance of environmentally sustainable methods. The recovery and recycling of silver from waste materials offer a promising approach to both reduce environmental pollution and create valuable nanomaterials for various applications.

Keywords: Silver nanoparticles, waste recycling, biogenic synthesis, antimicrobial properties, silver recovery, plant extracts, electronic waste, green chemistry, environmental sustainability, nanomaterials.

Introduction

Silver has been used extensively from last 5000 years for its antibacterial nature. Ag is preferred as nanoparticle for the reason that it has antibacterial property and non-toxic to human beings. Either killing or reducing the growth of bacteria without affecting surrounding cells is known as antibacterial activity. Various methods are used for preparation of silver nanoparticles like physical, chemical and biological. Demand of silver nanoparticle is increasing rapidly in many of the streams like in medical, pharmaceutical companies, healthcare, food, consumer, cosmetics etc.

Due to its uses it has been used for its several applications like antibacterial properties, household, medical devices, and food industry, wound dressing, in diagnostic, orthopaedics and an anticancer agent.[1] These nano-sized particles are found to be unique in nature and are also able to change their physical, chemical and biological property that's why they can be exploited in for various purposes. Various methods are used for the synthesis of these AgNP to fulfil the requirements of AgNPs.[2]

Normally, physical and chemical methods are found to be costly and dangerous. But the nanoparticles that are prepared from biological method they show high yield, high solubility as well as high stability. Out of all three methods biological method is found to be simple, environmental, commercial and single step method and doesn't need elevated temperature, pressure, force and deadly chemicals.[3]

Biogenic synthesis of AgNPs is an easy single-step protocol without generating harsh and toxic chemicals; hence, they are safe, economical and eco-friendly. In recent years, both plant and microbes are extensively investigated for the biosynthesis of AgNPs of varying size, shape, stability, and antimicrobial efficacy. Various parts of plant such as leaves, roots, flowers, fruits, rhizomes etc., have been successfully utilized for the synthesis of AgNPs.[4,5,6]

Silver containing materials arise from diversity of sources, such as manganese silver ore, refractory antimony ore, silver sulfide concentrates, lead–zinc sulfide concentrates, mining wastewater, spent photography/radiography films, electronic and electrical materials, waste jewelry, silver wares, brazing alloys, catalyst, batteries, dental amalgam, orthopedic materials, spent bleach-fixing photographic/radiographic solution, electroplating solution and metallurgical processing-solution are available in many forms. Processing of such sources is, therefore complicated. However, the basic processing technology is shown in Fig. 1. The pretreatment process involves washing, crushing, physical separation and incineration depending on the nature of materials and the metal obtained is of low purity. In the recovery process, such low purity metals are converted into crude silver by repeated leaching, adsorption or chemical reduction or cementation. Crude silver is subjected to the refining process to improve their purity to over 99.9%.[7]

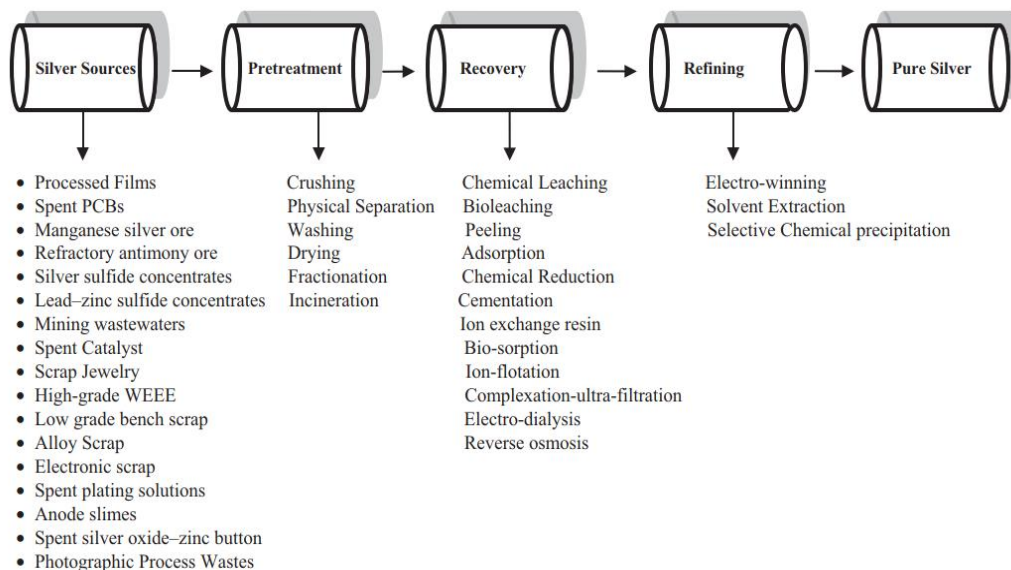


Fig. 1. Silver recovery and recycling basic process flow sheet.

Materials for Synthesis:

Preparation of AgNO_3 from electronic waste.

Electronic waste, including motherboards, circuit boards, and PCB boards, was collected from an electronic shop. The silver particles were extracted from this waste and weighed at 3.6 g using an electronic balance. The silver particles were then added to a solution of 0.5 M 70 ml HNO_3 acid and left to dissolve for three days to ensure complete dissolution of the silver particles. The resulting mixture was filtered and stored for further processing.

Preparation of pure AgNO_3 solution.

For pure AgNO_3 solution preparation, a 0.2 M AgNO_3 solution, 0.85 g of AgNO_3 powder, was taken and dissolved in 25 ml of deionized water.

Preparation of plant extract and green synthesis of silver nanoparticles.

Water hyacinth leaves were thoroughly washed with tap water to remove any dust and soil particles and were subsequently air-dried under sunlight for 3 days. Once dried, the leaves were ground into a fine powder, weighed at 3.036 g, mixed with 350 ml deionized water, and heated at 80°C while continuously stirring at 250 rpm for one hour. The resulting mixture was then filtered through filter paper, and the extract was stored at ambient temperature for further processing. This extraction process was conducted in accordance with standardized procedures to ensure the purity and efficacy of the resulting extract. The prepared plant extraction was used to reduce Ag ions from the AgNO_3 . To synthesize AgNPs, 30 mL of plant extract was treated with 30 mL of AgNO_3 (0.2 M) solution and allowed to react at room temperature for 1 h in direct sunlight. During this, the color of the reaction mixture was changed to brown, a color as an indication of the synthesis of AgNPs. [8,14-17].

Chemical synthesis of AgNPs from electric waste and pure AgNO_3 solution.

A 0.2 M solution of silver nitrate (AgNO_3) was loaded into a burette to synthesize Silver NP chemically.

In contrast, a conical flask containing a 0.2 M solution of sodium borohydride (NaBH_4) was prepared with an ice cube to lower the reaction rate. The AgNO_3 solution was then slowly added dropwise into the NaBH_4 solution.

To stabilize the synthesized AgNPs, 1% ascorbic acid was subsequently introduced into the solution.[18].

Silver recovery method from waste photographic films with NaOH stripping

The used X-ray films were washed with distilled water and wiped with cotton impregnated with ethanol, and were cut into 4 x 4 cm² pieces after being dried in an oven at 40°C for 30 min. Each of the films was weighed and stirred in series in a beaker containing 80 mL of 1.0-1.5 M NaOH solution at 70-80°C in a water bath until the gelatin-silver layer was stripped off completely. The resulting solution containing colloidal black metallic silver was stirred vigorously in a water bath at 90-95°C until coarse-grained silver was observed. The solution was easily decanted and the residue washed with distilled water, dried and weighed. The basicity of the used washing water was checked with a phenolphthalein indicator. The purity of the recovered silver was determined by potentiometric titration with a standard solution of NaCl using Ag/AgCl and a saturated calomel electrode as an indicator electrode and reference electrode respectively.[19] **Determination of trace metal impurities in the recovered silver.**

Sample cleaning

The recovered silver was transferred to a 100 mL PTFE beaker, and then 2.5 mL of cold 0.1 M HNO_3 was added and shaken for approximately 10 min. This was followed by a thorough rinsing in distilled water. It was then dried and stored in a desiccator.[20]

Sample pre-treatment

The cleaned silver was weighed and 3 mL of triply distilled water and 3 mL of concentrated nitric acid were added to it in a PTFE beaker. The sample was heated at temperatures below boiling point, and then 4 mL of 2.3 M HCl was added progressively to form a fine precipitate of silver chloride. After the addition of 2 mL of concentrated HCl and some 20 h of agitation, the solution was filtered by a G4 crucible under vacuum. The filtrate was made up to 25 mL triply distilled water in a calibrated flask, and then trace metals in the filtrate were determined by ICP-MS method.[20]

Recovery of Silver from Liquid Photographic Wastes

The extraction process was carried out by mixing an equal volume (25ml) of liquid photographic waste and unripe plantain peel ash solution using a mechanical shaker at a speed of 800rpm for 6 hours, after which the two phases separated. The supernatant phase was carefully decanted off into a clean specimen bottle. The sediment containing colloidal black gelatin layer was dried in an oven at a temperature of 80°C and later stored in a desiccator and kept away from light. This process was repeated for all concentrations of plantain ash solution. All experiments were carried out at ambient temperature (26°C).

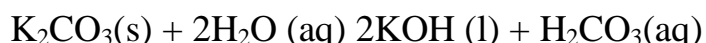
Recovery of Silver from Photographic and X-ray Films.

The used films of size 17.8 x 23.7cm² (i.e. X-ray films and photographic films) were washed with distilled water and wiped with cotton impregnated with ethanol and was cut into 2x2cm² after being dried in an oven at 60°C for 30 minutes. The films were weighed and stirred in series in a beaker containing 150ml of various concentrations of unripe plantain peel ash solution for the 10g-200g ash at 100°C in a water bath until the gelatin silver layer is stripped off completely (Nuri et al 2003).

The stripped films were carefully transferred into a clean beaker, dried and weighed. The resulting solution was stirred vigorously in a water bath at 100°C until coarse – grained substance was observed. The solution was carefully transferred into an evaporating dish and heated to dryness. The dish and its content were weighed and stored in a desiccator and kept away from light. The time taken for complete stripping at different concentrations of plantain ash solutions was recorded. Complete stripping of the film was indicated by the appearance of a clear white colouration (for photographic film) or a light blue colouration (for X-ray) film. This process was repeated for all concentrations of the plantain peel ash solution.

Test for Silver

The recovered product was tested for silver ion using the streak test with nitric acid and potassium chloride. UV-visible Analysis: 1.0g each of the recovered product from the various photographic wastes was weighed and dissolved in 5ml deionized water and 10ml concentrated HNO₃ and made up to 100ml with deionized water. 0.4M-4.0M solutions of analar grade AgNO₃ was prepared for the absorbance measurement at a wavelength of 380nm and path length of 1cm. Table 1 confirms the alkaline solution of PAS. pH values range from 10.2 to 11.2. Plantain peels ash like most land plants contain potassium carbonate. Therefore, the ash in solution produces potassium hydroxide (KOH) according to the equation;



The resulting solution will be more alkaline since H₂CO₃ is a weak acid and only feebly ionized. As expected, the concentration of PAS increased with increase in quantity of ash dissolved. Silver recovery: As reported in our previous paper (Orubite and Jack 2011) complete stripping was achieved at temperature range 80 – 100°C for x-ray and photographic film. It was observed that the higher the quantity of PAS the shorter the stripping time. This may be attributed to the fact that more hydroxyl ions are available for reaction with the silver ions. Test for silver ion: The appearance of a milky precipitate was observed as a proof for the presence of silver in all the products obtained. Measurement of silver ion: The calibration curve for AgNO₃ is shown in Graph 1 The absorbance measurement for silver ion in each recovered product is recorded in Table 3. From the calibration curve obtained for silver nitrate the concentrations of silver ion in the products were determined by extrapolations (Table 4). As shown in Table 4 highest amount of silver ion recovered was in the photographic film (7.72M) when PAS concentration of 0.2930M was used. X- ray films also recorded the highest amount of silver ions (3.12M) at this same PAS concentration.

For the solutions (stabilizer and fixer), highest amounts of silver ion were recorded for PAS concentration between 0.5690 - 0.8450M (Fixer solution 6.38M and stabilizer solution 0.372M). From the PAS concentrations mentioned so far it is evident that more silver ions were obtained in the films than the solutions. This could be attributed to the different sources they were collected. The solutions were used to wash photographic films before collection while the films were stripped of the silver in the laboratory. There is no knowledge of number of films that had been washed in them before collection. It is therefore difficult to conclude that the films contain more silver ions than the photographic solutions. For the purposes of the research since equal volumes of solutions were used the comparison can be based on that. Again, the methods of recovery may have contributed to the significant difference in the amount of silver ion in the two sources. The films were stripped with PAS to obtain the product while for the solutions direct precipitation was done with the PAS solution. In all it is noteworthy that PAS extracted silver ions from the various wastes. Generally, in all the wastes, table 4 also reveals that lower concentrations of silver ions were obtained in higher concentrations of PAS. Thus, for PAS concentration of 2.0792 M and 2.7670M all the various wastes recorded low concentration of silver ions extracted. This trend may be attributed to the complex formation property of the silver ion. Essentially all of the silver may have been present as the Ag^+ ion at very low concentrations of PAS. As the PAS concentration increased, the dominant species soon became the two-coordinate $\text{Ag}(\text{OH})_2^+$ ion which is not available as silver ion, hence the low concentration of silver ion recorded. From the above it follows that the observation that higher conc. of PAS correspond to faster stripping time is not a means to obtaining more silver ions. At these high PAS concentrations complex ions are rather in existence in the solutions. [21]

Table 1. Concentration of unripe plantain ash solution (PAS)

Conc of acid (M)	Amt of PAS (g) in 500ml sol	pH of unripe PAS sol	1st Titre (cm^3)	2 nd Titre (cm^3)	3 rd Titre (cm^3)	Vol of acid used	Conc of PAS	Acid used HCl indicator methyl orange
1.0	10.00	10.7	3.70	3.80	3.75	3.75	0.1500	
1.0	20.00	11.0	7.30	7.30	7.40	7.33	0.2930	
1.0	30.00	11.1	10.70	10.80	10.80	10.77	0.4310	
1.0	40.00	11.2	14.25	14.20	14.25	14.23	0.5690	
1.0	50.00	11.2	17.80	17.90	17.90	17.87	0.7150	
1.0	60.00	11.0	21.15	21.10	21.10	21.15	0.8450	
1.0	100.00	10.4	34.77	34.87	34.82	34.82	1.3930	
1.0	150.00	10.2	51.93	52.03	51.98	51.98	2.0792	
1.0	200.00	10.4	69.10	69.20	69.25	69.18	2.7670	

Table 2

PHOTOGRAPHIC FILM		X-RAY FILM	
PAS conc.(M)	TIME (Min)	PAS conc.(M)	TIME (Min)
0.1500	142	0.1500	200
0.2930	122	0.2930	186
0.4310	98	0.4310	160
0.5690	68	0.5690	120
0.7150	52	0.7150	104
0.8450	44	0.8450	98
1.3930	38	1.3930	64
2.0792	30	2.0792	55
2.7670	25	2.7670	48

Graph 1. Calibration curve for AgNO_3

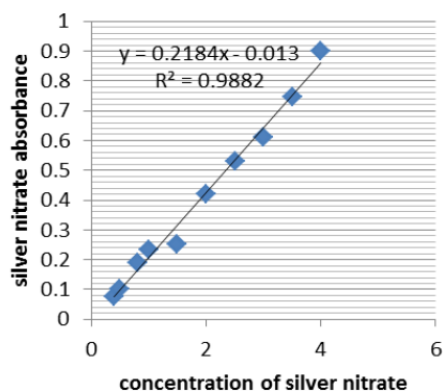


Table 3. Absorbances of recovered products from UV analysis

Absorbances of recovered products from UV analysis (Wavelength 380nm and 1cm pathlength)				
Conc of PAS	Fixer solution	Stabilizer solution	Photographic film	X- ray film
0.1500	0.6611.	1.500	1.434	0.591
0.2930	0.837	0.990	1.636	0.664
0.4310	0.447	1.190	1.568	0.177
0.5690	0.543	1.75	1.372	0.301
0.7150	0.959	1.192	1.479	0.170
0.8450	1.346	1.250	0.926	0.226
1.3930	0.446	1.550	0.626	0.128
2.0792	0.155	0.650	0.683	0.124
2.7670	0.246	0.100	0.363	0.120

Table 4. Concentrations of silver ion in the products

Conc.of PAS	Fixer solution	Stabilizer solution	Photographic film	X- ray film
0.1500	3.100	0.309	6.750	2.770
0.2930	3.990	0.198	7.720	3.120
0.4310	2.150	0.238	7.420	0.855
0.5690	2.570	0.372	6.48	1.45
0.7150	4.55	0.239	7.000	0.850
0.8450	6.380	0.262	4.380	1.080
1.3930	2.149	0.315	2.950	0.62
2.0792	0.780	0.129	3.220	0.58
2.7670	1.180	0.025	1.72	0.56

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