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Synthesis, Characterization and Selective Heavy Metal Removal Property of Silver Nanoparticles from Leaf Extract of *Aerva lanata*

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ABSTRACT

The adsorption process by silver nanoparticles has been investigated an effective agent for removing selective heavy metals from the industrial wastewater. In this study, silver nanoparticles were synthesized in the presence of *Aerva lanata* leaf extract as adsorbent for copper and Zinc ions removal from industrial waste water solution. silver nanoparticles prepared by co-precipitation method and *Aerva lanata* leaf extract was used to prevent accumulation and reduce the diameter of the particles. Silver nanoparticles were characterized by Scanning Electron microscope (SEM), Transmission electron microscopy (TEM). Effect of various parameters such as contact time, pH, metal concentration and adsorbent dosage was determined on the removal efficiency by using atomic absorption spectrophotometer. Based on the present investigation, it could be concluded that some low-cost materials like *Aerva lanata* silver nanoparticles can be used efficiently in the removal of Heavy metal ions (Cu_2^+ and Zn_2^+) from effluent. The removal of heavy metal ion was pH dependent as the adsorption capacity increases with increasing the pH value of the solution, and at a particular pH the order of increasing the removal percentage was $\text{Zn} < \text{Cu}$. Experimental results showed that the best pH was 4 and time was 90 min. The metal ions showed different behaviors towards on *Aerva lanata* silver nanoparticles by increasing the initial concentration of the metal ions. The copper and zinc ions are usually soluble in acidic pH and the maximum removal of cadmium by green synthesis silver nanoparticles was obtained in the pH of 4, so these nanoparticles can be a good adsorbent for the removal of heavy metal removal from wastewater.

Key words: Silver nanoparticles, Heavy metal removal, *Aerva lanata*, Leaf extract

Nanotechnology is a broad interdisciplinary area of research, development and industrial activity which has grown very rapidly all over the world for the past decade. Different techniques like ultraviolet irradiation, aerosol technologies, lithography, laser ablation, photochemical reduction have been used to produce metal nanoparticles [1-2]. Most of the methods reported in the literature are extremely expensive and also involve the use of toxic, hazardous chemicals such as stabilizers which may pose potential environmental and biological risks. Because of the increasing environmental concerns by chemical synthesis routes, an environmentally sustainable synthesis process has led to green approaches, which refers to applying biological principles in materials formation [3].

The use of plant extracts to synthesize nanoparticles is receiving attention in recent times because of its simplicity. Also, the processes are readily scalable and may be less expensive. Plant extracts may act both as reducing agents and stabilizing agents in the synthesis of nanoparticles. Nowadays, the preparation of nano-scaled silver and gold materials has become very important due to their unique properties, which are different from those of the bulk materials [4]. The properties of these particles in applications as diverse as catalysis, sensors and medicine depend critically on the size and composition of the nanoparticles [5-6]. Production of nanoparticles can be achieved through mainly three methods such as, chemical, physical and biological methods. Since noble metal nanoparticles such as gold, silver and platinum nanoparticles are widely applied to human contacting areas, there is a growing need to develop environmentally friendly processes of nanoparticles synthesis that do not use toxic chemicals. Biological methods of nanoparticles synthesis using microorganism, enzyme, and plant or plant extract have been suggested as possible eco-friendly alternatives to chemical and physical methods [7-10]. Specifically, the study has been attempted bioreduction of chloroaurate ions or silver ions by the broths of geranium and neem [11]. Also, gold nanotriangles synthesized using Tamarind leaf extract and studied their potential application in vapour sensing [12]. Recently, a study

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has been demonstrated synthesis of gold nano-triangles and silver NPs using aloe vera plant extracts [13]. Already some works have been reported on synthesis of gold nanoparticles by boiled leaf extract of *Azadirachta indica* [14]. In the present study we have investigated biosynthesis and characterization of silver nanoparticles by fresh leaves of *Aerva lanata*.

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electrolytes depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals wastes results from printed circuit board (PCB) manufacturing. Tin, lead, and nickel solder plates are the most widely used resistant over plates. Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferro cyanide. All of these generators produce a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes requiring extensive waste treatment [15-16].

Aim of the study was to produce the crude extraction of *Aerva lanata* by maceration extraction procedure. In the present study, attempt has been made to identify the bio-active ingredients present in the leaf extracts of *Aerva lanata* plant was subjected to synthesis and characterization of silver nano particles and heavy metal removal studies by using the following steps. Preparing commercial leaf powder of *Aerva lanata*, leaf extraction by using silver nitrate solution, synthesis and characterization of silver nano particles and Heavy metal removal study.

RESULTS AND DISCUSSION

Preparation of plant extract

The leaf sample of *Aerva lanata* was collected from the Cheyyar, Tamil Nadu. Random leaf samples were collected into plastic zip lock bags with appropriate labeling and stored in an ice box until being transported to the laboratory for extraction.

Extraction methods used form plant extract

The leaf *Aerva lanata* of samples were washed in tap water, dried, and placed into a blender to be grounded into powder. The distilled water was added were used for the maceration extraction procedure. The leaf powder was added to double distilled water to make a 10% concentration. The mixtures were made in sterile 250 mL Erlenmeyer flask wrapped in aluminum foil to avoid evaporation and boiled for 10 min and cooled at room temperature. The flasks were placed on a platform shaker at 700 rpm for 1 h. After incubation the mixture was filtered through Whatman Filter paper No. 1 and the supernatant was collected and stored at 4 °C until use.

Green synthesis of silver nanoparticle using silver nitrate procedure

10 ml of 1mM silver nitrate was prepared from 10 mM stock of silver nitrate solutions with distilled water and different combination of leaf extract was added with metal salt solution and make up to a total of 10 ml individually. The combination

was selected as 1:9, 2:8, 3:7, 4:6, and 5:5 as silver nitrate and leaf extract, respectively. The combined solutions were kept at least 4 h in dark light. The reduction of nanoparticle was observed using the color change of the solution and reduction of pH value of the entire solution. After nanoparticle synthesized, they were centrifuged at 5000 rpm for 15 min. The pellet were washed with distilled water thrice and centrifuged. The thrice washed pellet was dried in air and subjected to biological properties analysis and spectral analyses.

Spectral determination

Scanning electron microscopy (SEM)

Scanning electron microscopy was performed JEOL 2100 Field Emission gun-based Scanning Electron High Solution Microscope (FESEM). The powdered nanoparticle was place on double side adhesive tape and recorded without any sputter coating.

Transmission electron microscopy (TEM)

TEM analysis was performed to characterize the size and shape of the green synthesized silver nanoparticles. TEM analysis was done using the JEOL 3010 instrument operating at 200 kV.

Metal analysis

The metals in the waste water were analyzed using Atomic Absorption Spectroscopy (Varian Model SPECTRAA 220) using Indian Standard methods of sampling and test (physical and chemical) for water and wastewater.

Industrial waste water treatment

The waste water was treated with 0.1% biologically synthesized silver nanoparticle and kept for 24 and 48 h in shaking condition (Rivotech, Orbital shaker, Mumbai) at 100 rpm. After incubation the treated water 24, 48 h samples were taken for centrifugation at 5000 rpm for 10 min. The resultant supernatant were collected in a clean plastic container and tested for zinc and copper, Chromium, Lead.

RESULTS AND DISCUSSION

SEM analysis

The morphological features of synthesized silver nanoparticles from *Aerva lanata* extract was studied by Scanning Electron Microscope. The figure 1 shown the high density of AgNPs has confirmed the presence of AgNPs. The electrostatic interactions such as hydrogen bond, bio- organic bond and capping molecules are the reason for biosynthesis of silver nanoparticles [17]. The Synthesized nanoparticles were spherical and rod shape. Silver nanoparticles in the average range of 600 nm. The size was more than the desired size as a result of proteins which were bound in the surface of the nanoparticles. The shape may vary due to the concentration profile [18].

Transmission electron microscopy

TEM images of silver sol are shown in (Fig 2). These observations indicate the adsorption and/or deposition of silver nanoparticles onto the surface of roughly sphere-shaped polydispersed particles for $[Ag^+] / [aniline]$ ratios of 0.8, 0.4 and 0.3, respectively.

The Ag- nanocrystals that emerged in the images have variety of shapes: spherical, triangle and irregular, presence of rings patterns in the selected area electron diffraction reveals the single face-centered cubic (fcc) crystalline nature of the spherical nanoparticles with a preferential growth direction

along the Ag (110), (200), (220), (311) and (331) planes. In agreement with the UV-VIS spectrophotometric observations, the TEM images reveal Ag-nanocrystals are polydisperse, irregular deposition and roughly spherical of a rather similar diameter 25 nm. Our results are quite consistent with that for

the synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity suggested that faceted or rodlike nanoparticles are formed during the reduction of metal salts by weak reducing agents where growth occurs over a longer period.

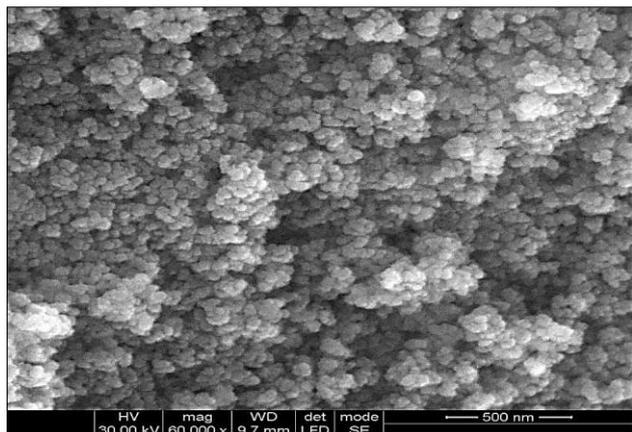


Fig 1 Scanning electron microscopy

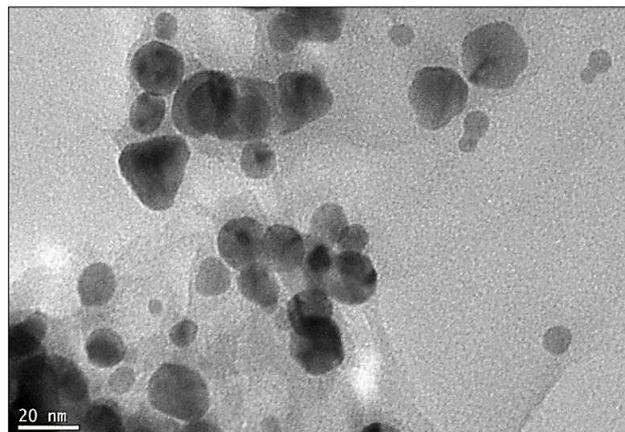


Fig 2 Transmission electron microscopy (TEM)

Effect of mass of *Aerva lanata* silver nanoparticle: The removal of the heavy metal ions

The pH of the industrial waste water solution was adjusted to 4. To 50 mL of the industrial waste water, 0.2, 0.4 and 0.6 gram of the *Aerva lanata* silver nanoparticle were added in an Erlenmeyer flask, and the mixtures were shaken using a rotary shaker at about 200 rpm for 120 min. After that the mixtures were filtered using a Whatman no. 1 filter paper. The filtrate and the industrial waste water were analyzed using an atomic absorption spectrophotometer. Each experiment was

carried out at room temperature and was repeated two times, and the results are given as averages. The effect of weight of *Aerva lanata* silver nanoparticle plant on the percent removal of Cu_2^+ and Zn_2^+ is shown graphically in (Fig 3). Inspection of the data obtained showed that:

Maximum percent removal was obtained for Cu_2^+ ions, which is nearly equal to 80 % which is slightly increased by the increase in the weight of sorbent. Minimum removal was obtained for Zn_2^+ ion, which is slightly increased by the increase in the weight of sorbent.

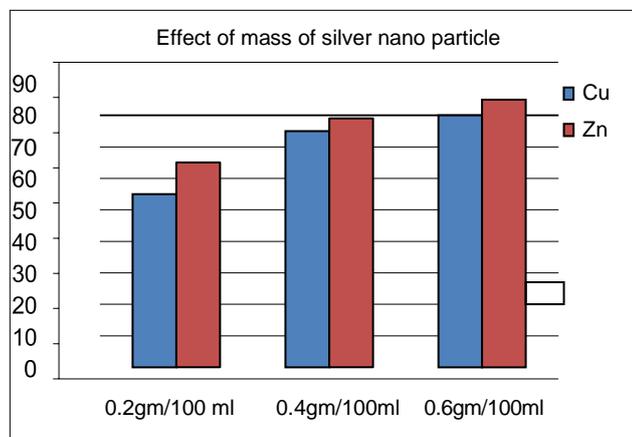


Fig 3 Effect of mass of *Aerva lanata* silver nano particle

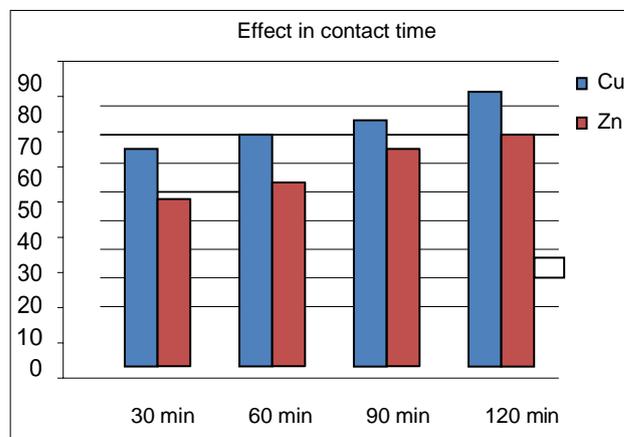


Fig 4 Effect in contact time

Effect of contact time on the removal of the heavy metal ions

To 50 mL Industrial waste water, 0.6 gram of the *Aerva lanata* silver nanoparticle were added and the mixtures were shaken for 30, 60, 90 and 120 minutes, and analyzed using an atomic absorption spectrophotometer. Adsorption Cu_2^+ and Zn_2^+ ions were measured at given contact times. The plot revealed that the rate of percent metal ions removal is higher at the beginning. This was probably due to larger surface area of the plants being available at beginning for the adsorption of Cu_2^+ and Zn_2^+ ions. As the surface adsorption sites become exhausted, the uptake rate was controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Most of the maximum percent Cu_2^+ and Zn_2^+ removal was attained after about 120 min of shaking time. Results of studies on the effect of Contact time on the

maximum removal of the metal ions under investigation, illustrated in (Fig 4).

Effect of pH on the removal of the heavy metal ions

The adsorption of Cu_2^+ and Zn_2^+ ions were found to be strongly dependent on the pH of the solution and analyzed using atomic absorption spectrophotometer. It was demonstrated that the optimum pH for the adsorption metal ions were about 4 which were rather acidic. At low pH (below 3), there was excessive protonation of the active sites at *Aerva lanata* nanoparticle powder surface and this often refuses the formation of links between metal ions and the active site. At moderate pH values (3 to 6), linked H^+ is released from the active sites and adsorbed amount of metal ions is generally found to increase (Fig 5). Moreover, at higher pH values (above

6), the precipitation was dominant or both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process. In practice, metal precipitation is generally not a stabilized form of heavy metal

as the precipitation can sometimes be very small in size, and upon the neutralization of the effluent from the wastewater treatment plant, the solubility of the metals increases resulting in a recontamination of the waste outlet stream.

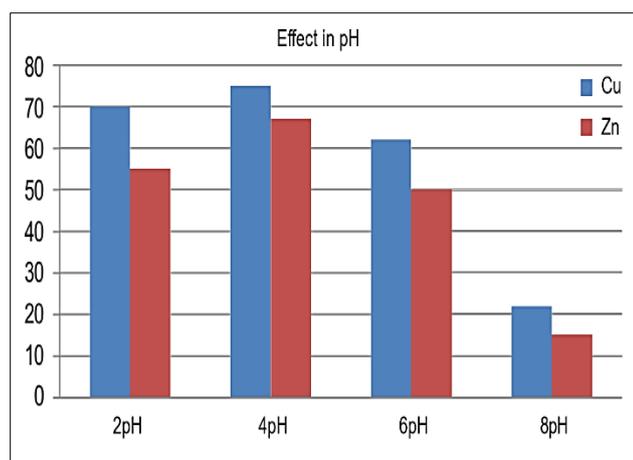


Fig 3 Effect of pH

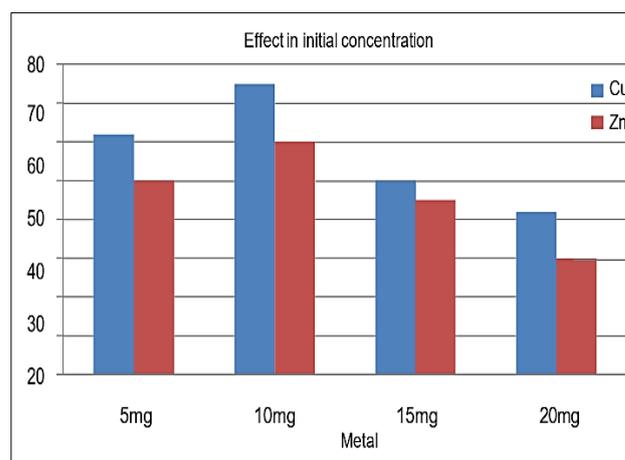


Fig 6 Effect in initial concentration

Effect of initial concentration of the heavy metal ions on the removal percentage

A standard solution with concentrations of 5, 10, 30 and 50 mg/L were prepared. The solutions were treated as previously and analyzed using atomic absorption spectrophotometer. The variation of percent removal with change in initial concentration of heavy metal ions showed regular trend. The percent removal for metal ions increases with increasing the initial concentration, till reaching 10 mg/L, then decreases as the initial concentration increases up to 50 mg/L. The results are present in (Fig 6).

CONCLUSION

The use of *Aerva lanata* silver nanoparticle as stabilizer agent for preparation of silver nanoparticle is inexpensive, and eco-friendly. It is especially for preparation of nanoparticles that have been free of toxic contaminations. The *Aerva lanata* extract can controlled the size and morphology of nanoparticles during synthesis process. Simple green synthesis of silver nanoparticles through co precipitation in alkali condition can exhibit an excellent adsorption for the metal ions. Based on the

present investigation, it could be concluded that some low-cost materials like *Aerva lanata* silver nanoparticles can be used efficiently in the removal of Heavy metal ions (Cu_2^+ and Zn_2^+) from effluent. The removal of heavy metal ion was pH dependent as the adsorption capacity increases with increasing the pH value of the solution, and at a particular pH the order of increasing the removal percentage was $\text{Zn}_2^+ < \text{Cu}_2^+$. Experimental results showed that the best pH was 4 and time was 90 min. The metal ions showed different behaviors towards on *Aerva lanata* silver nanoparticles by increasing the initial concentration of the metal ions. This investigation also showed silver nano particles prepared from *Aerva lanata* to be suitable nanoparticle for removing Cu_2^+ and Zn_2^+ heavy metal ions. The experimental studies showed that *Aerva lanata* silver nanoparticle could be used as an alternative, inexpensive and effective material to remove high amounts of toxic heavy metal ions from waste water.

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