GREEN SYNTHESIS AND CHARACTERIZATION OF TRIMETALLIC ALLOY NANOPARTICLES

Abstract

Crystallized Manganese (Mn), Nickel (Ni), Zinc (Zn) tri-metallic alloy nanoparticle have been prepared and stabilized using plant extracts of *Caparis Zylanica* leaves in an aqueous system. Aqueous solutions of Mn^{+2}, Ni^{+2}, Zn^{+2} ions are in 1:1:1 volume ratio of Mn-Ni-Zn alloy was treated with a filtered solution of *Caparis Zylanica* leaves extract for the formation of Mn-Ni-Zn tri-metallic alloy nano particles (Mn-Ni-ZnNPs). Analysis of the feasibility of the biologically synthesized bio-functional nanometal alloy from plant leaves extract is particularly noteworthy. The colloidal suspensions obtained were in stable condition for 2-3 weeks. The composition, morphology, size and structure of the nanoparticles were determined by UV-Visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM).

Keywords: Trimetallic alloy nanoparticles, Capparis zeylanica, UV-Visible, FTIR, SEM.

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I. INTRODUCTION

Novel synthesis techniques for nanomaterials have been a fascinating field in nanoscience and technology during the last decade. Nanoparticles are incredibly small particles between 1-100 nm in size, either created naturally or artificially. They display special and important chemical and physical characteristics. The catalytic, magnetic, electrical, mechanical, optical, chemical, and biological characteristics of particles are improved at the nanoscale. Nanoparticles have increased reactivity, mobility, dissolving characteristics, and strength because of their high surface to volume ratio [1]. Four main categories of nanoparticles are defined based on their chemical composition, including carbon-based, metal and metal oxide-based, bio-organic based, and composite based [2]. Nanoparticles may also be classed as organic and inorganic in origin [3]. While inorganic nanoparticles are based on inorganic materials made of metals and metal oxides like silver oxide, zinc oxide, etc., organic nanoparticles are biodegradable in nature and include polymeric nanoparticles, lipid-based nanocarriers, liposomes, carbon-based nanomaterials, and solid lipid nanoparticles.

Two alternative fundamental concepts of synthesis, such as top down and bottom up techniques, have been studied in the literature in order to produce nanomaterials with the appropriate sizes, shapes, and functions. In top-down procedures, nanomaterials are created using a variety of synthesis techniques [4], whereas in bottom-up methods, nanoparticles are created by growing them from smaller molecules. Biological processes are used in green nanoparticle manufacturing, which is more effective than other similar procedures and produces particles with a larger mass. In order to synthesise green nanoparticles, stabilising and reducing agents can be produced from a variety of biochemicals and components found in plants. When compared to alternative biological, physical, and chemical approaches, the green synthesised processes are more stable, non-toxic, cost-effective, and environmentally friendly [5]. The green synthesis technique was utilised to create nanoparticles utilising a variety of plants. In comparison to microorganisms, plants create nanoparticles that are more stable and synthesise them at a faster rate.

Due to the abundance of potent phytochemicals in various plant extracts, particularly in leaves like ketones, aldehydes, flavones, amides, terpenoids, carboxylic acids, phenols, and ascorbic acids, plant biodiversity has received considerable attention for the synthesis of metal/metal oxide nanoparticles. These compounds have the ability to convert metal salts into metal nanoparticles [6]. Researchers are interested in studying the mechanisms of metal ions absorption and bioreduction by plants, as well as the potential mechanisms of metal nanoparticle creation in plants, due to the benefits of employing plants and materials generated from plants for the biosynthesis of metal nanoparticles. The *Capparis zeylanica* leaf was selected for synthesis in this experiment. It is a member of the Capparidaceae family and is found all over the world, including Bangladesh, Pakistan and Ardanda. It has historically been used to treat a number of conditions, including snake bites, testicular edoema, boils, small pox, cholera, ulcers, hemiplegia, neuralgia, pnemoniae, and pleurisy [7]. It was proven to have anti-inflammatory, analgesic, antioxidant, antipyretic, antibacterial, and immune stimulant properties. Phytochemical analysis of the plant revealed the presence of fatty acids, flavonoids, tannins, alkaloids, saponins, glycosides, terpenoids, saponin, p-hydroxybenzoic, syringic, vanillic, ferulic, and p-coumanic acid [8-10].

The *Caparis zeylanica* leaves were used in this work for the synthesis of tri metallic alloy nanoparticles, since it has not been reported for synthesis of trimetallic alloy nanoparticles. As a result, the current work intends to synthesize and characterize nanosized trimetallic alloy (Mn-Ni-ZnNPs) nanoparticles from the leaves of Caparis zeylanica.

II. MATERIALS AND METHODS

Materials

1. **Plant:** Capparis zeylanica plant leaf was collected from Thirumayam, Pudukkottai, Tamilnadu, India.

2. **Chemicals:** The chemicals namely, Manganese sulphate, Nickel chloride, Zinc sulphate were obtained from Sigma Aldrich chemicals India and used as without further purification. Double distilled water was used throught the process. Whatman no.1 filter paper was used for filtration. Glassware used for the complete reactions were washed well and rinsed with double distilled water and dried in hot air oven before use. The metal salt solutions used were 0.1M Manganese sulphate-$MnSO_4$, 0.1M Nickel chloride-$NiCl_2$, 0.1M Zinc sulphate-$ZnSO_4$

3. **General Information of Plant:** Capparis zeylanica is an evergreen climbing shrub producing stems 2-5 meters long, occasionally to 10 meters. The plant is harvested from the wild for local use as a medicine and occasionally as a food. Beautiful flowers, which are essentiality a spreading spray of pink-white stamens and appear solitary in leaf axils. The flowers turn dark pink while fading.

Table 1: General Information of plant

Scientific Classification	
Kingdom	Plantae
Phylum	Tracheophyta
Class	Magnoliopsida
Order	Capparales
Family	Capparaceae(caper family)
Genus	Capparis
Species	Capparis zeylanica.L
Common name	Ceylon coper,Indian caper
Tamil name	Adondai, Karrottai

Methods

1. **Preparation of Extract:** The bottom up bio synthesis method is used. The extract was prepared by modifying the method reported by Saranyadevi K et.al [11].The *Caparis zeylanica* leaves were washed several times with water and rinsed with deionized water for the removal of impurities. 10g of sliced *Capparis zeylanica* leaves was weighed then boiled with deionized water for 10 minutes and was filtered using Whatman No.1 filter paper. The filtrate was collected in clean, dry conical flask and kept for further use.

2. **Synthesis of Mn-Ni-Zn Nanoparticles:** The tri metal alloy of Mn-Ni-Zn nanoparticle was prepared by mixing (1:1:1volume ratio) 25ml of 0.1M each of these salts solution, which is of Manganes sulphate, Nickel chloride and Zinc sulphate. Then 25ml of extract was added and a colour change was observed from pale yellow to reddish and then turned darker and kept at room temperature which indicates formation of Mn-Ni-Zn trimetallic alloy nanoparticles. Then the solution was centrifuged at 6000 rpm for 15min and the sample was sent for characterization tests which are UV-visible spectroscopy, FTIR, SEM.

3. **Characterization:** The UV-Visible spectral measurements were used to confirm the formation of Mn-Ni-Zn nanoparticles by using PERKIN ELMER-UV-WIN spectrophotometer instrument in the range between 200-800nm [12]. FTIR experiment to be carried out to determine the biomolecules present in the leaf extract responsible for the reduction of Mn-Ni-Zn ions with 400-4000cm^{-1} of spectra range. The sample was centrifuged at 9000 rpm for 15min, then dried and ground with KBr pellet and analyzed on PERKINELMER-FTIR model. The sample were prepared on a carbon coated grid by just dipping a very small amount of the prepared Mn-Ni-ZnNPs on grid, by using blotting paper the extra solution was isolated, then the sample were allowed to dry for SEM analysis using Suprazeis with resolution of 1nm at 30kV with 20mm Oxford EDS detector.

Figure 1: Synthesis of Nanoparticles

4. **Phyto Chemical Screening:** Qualitative phytochemical of the following tests were performed on extracts to detect various phytochemicals present in them [13].

Table 2: Phyto chemical Screening analysis of plant material

Test	Specific Test	Reagent Composition	Observed Color	Inference
Detection of Flavonoids	Ferric chloride Test	Solution when treated with a drop of Ferric chloride	Blackish red color	Presence of Flavonoids
Detection of Alkaloids	Mayer's Test	Extract mixed with ammonia and then with chloroform solution. Dil HCl was added. Acid layer with a few drops of Mayer's reagent.	Creamy white precipitate	Presence of Alkaloids
Detection of Tannins	-	5ml of extract, $FeCl_3$ was added.	Deep blue (or) greenish black color	Presence of Tannins
Detection of Glycosides	Keller killani's Test	Dissolved the extract in water with glacial acetic acid, $FeCl_3$,Con.H_2SO_4	Brown ring	Presence of Glycosides
Detection of Steroids	Salkowski's of Steroids	2ml of extract, 2ml of chloroform was added, followed by 3ml of H_2SO_4.	Reddish brown color	Presence of Steroids
Detection of Phenols	-	Extract was dissolved in 5ml of distilled water. Few drops of neutral 5% $FeCl_3$ solution was added.	Dark green color	Presence of Phenolic Compound.
Detection of Saponins	-	A pinch of dried powdered plant was added to 2-3 ml of distilled water. The mixture was shaken vigorously	Formation of foam on surface	Presence of saponins
Detection of Carbohydrates	Molish Test	Powdered plant extracts 1ml of napthol solution.con. H_2SO_4 was added to the sides of test tube	Purple (or) reddish Violet color	Presence of Carbohydrates
Detection of Proteins	Xanthoprotein Test	Few mg of powder 1ml of Con.HNO_3 was added. It was then boiled and cooled	White precipitate	Presence of Proteins
Detection of Amino acid	-	3ml of test solution and 3 drops of 5% Ninhydrin solution were added in test tube and heated in water bath for 10 minutes.	Purple (or) bluish Color	Presence of Amino acid

III. RESULTS AND DISCUSSION

1. **UV-Vis Spectroscopy Analysis:** The change in colour of the mixture from pale yellow to reddish brown within few minutes indicates the formation of metal alloy Mn-Ni-Zn nanoparticles. On allowing the solution for a day, it becomes darker solution than previous colour. UV-Visible spectroscopy analysis of plant extract and Mn-Ni-Zn nanoparticles was confirmed and shown in Figure 2(a) and 2(b).When the plant extract was added into the Mn-Ni-Zn solution the pale yellow color was obtained. After 20 minutes, the colour changes from pale yellow to dark reddish brown. The absorption spectra of Mn-Ni-Zn nanoparticles formed in the reaction mixture was obtained by the UV-Vis analysis at the range between 200-800nm, the Mn-Ni-ZnNPs has sharp absorbance with highest peak at 268nm progressively decreased while increased [14]

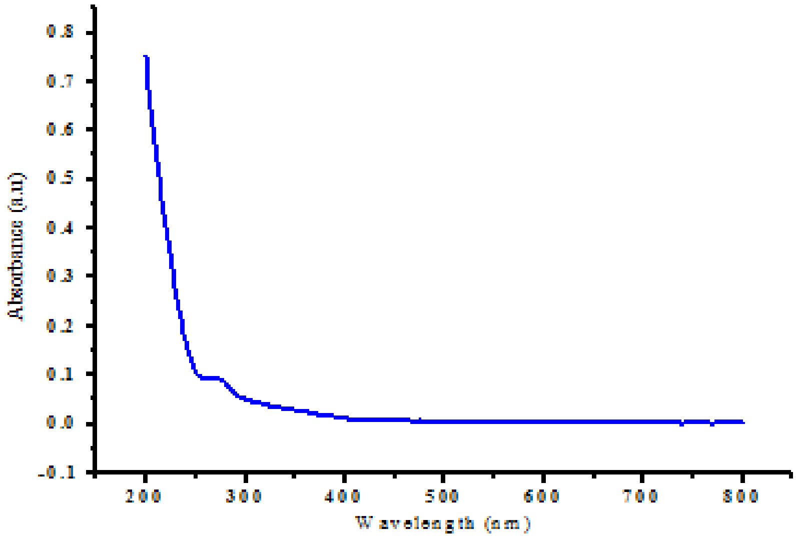

Fig. 2(a). UV-Visible Spectrum of Extract

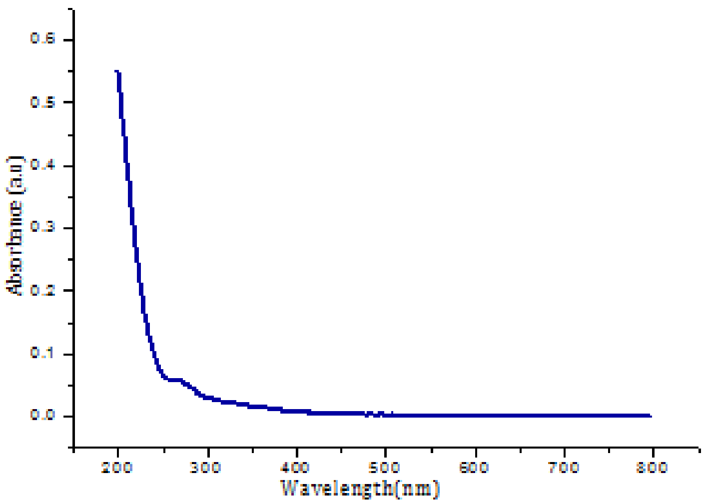

Fig.2(b).UV-Visible Spectrum of Extract and Mn-Ni-Zn metal Solution

2. **FTIR Analysis:** FTIR measurement was done to identify the reducing, capping and stabilizing capacity of *Capparis zeylanica* leaf extract. The FTIR analysis was done for

both plant extract and Mn-Ni-Zn NPs. In Figure 3(a), aqueous plant extract shown the peaks at 1636cm^{-1} , 2119.75cm^{-1} , 3331.76cm^{-1}, 592cm^{-1} the peak at 2119.75cm^{-1} shows the bondsdue to corresponds in alkynes [15] and 3331.76cm^{-1} corresponds to O-H stretching of carboxylic acid stretching like galic acid, acetic acid and gibberllic acids;1636cm^{-1} C=O stretching [16], 592cm^{-1} C-Cl stretching, peak at 1636cm^{-1} was a strong absorption peak which indicates the characteristics IR absorption of polysaccharides shows the bonds due to C=O stretching of amines [17]. Whereas the Mn-Ni-Zn nanoparticles present in the solution shows the peak at around 1637, 2123.39, 3331.73, 592.5cm^{-1}in figure 3(b). The peak at 2123.39cm^{-1} corresponds to alkyne stretching of phenolic compound, where as other peaks 3331.73cm^{-1} obtained in Mn-Ni-Zn metallic alloy nanoparticles due to O-H stretching of hydroxyl groups [18, 19]. Particularly the plant leaves contained the chemical constituents of phenolic compounds, alkaloids and fatty acids such as thioglycoside, β-carotene, glycocapparin, α-amyrin are acting as capping and reducing agents [20].

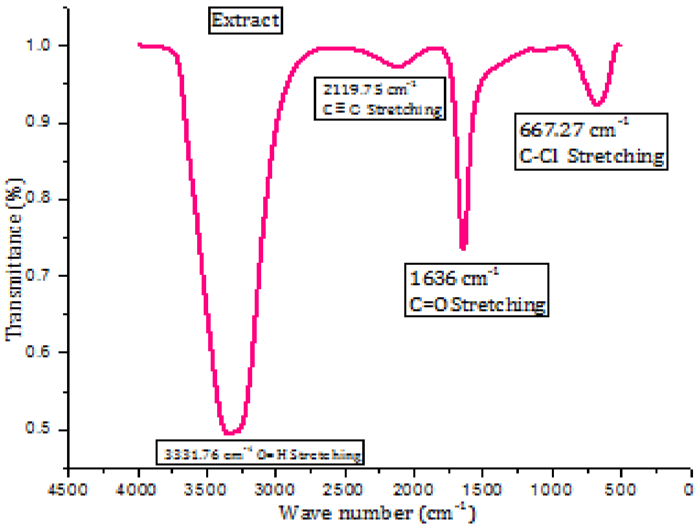

Fig. 3(a)- FT-IR Spectrum of plant extract

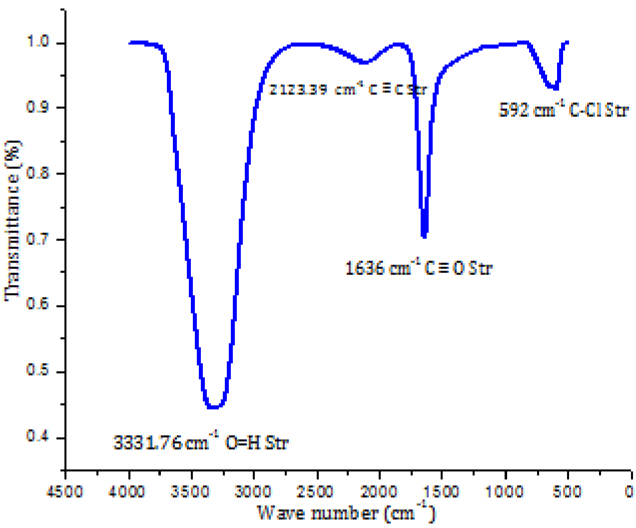

Fig. 3(b). FT-IR Spectrum of synthesised Mn-Ni-Zn nanaoparticles

3. **Scanning Electron Microscopy (SEM) analysis:** The surface morphology of Mn-Ni-ZnNPs was analyzed by scanning electron microscope it was performed by EVO-18 CAREL ZEISS model an operating on the voltage of 10 kV and for operation need a very small amount of dry powder sample put on a grid and removed excess sample with the help of blotting paper. Shape and morphology of the synthesized nanoparticles were identified by scanning electron microscope analysis. Then nanoparticles were examined under various magnifications of X10,000, X25,000, X35,000 and X45,000 SEM images of the synthesized Mn-Ni-ZnNPs are shown in Fig.4. It was shown that spherical and relatively uniform shape of the Mn-Ni-Zn trimetallic alloy nanoparticles in the range 128-169 nm.

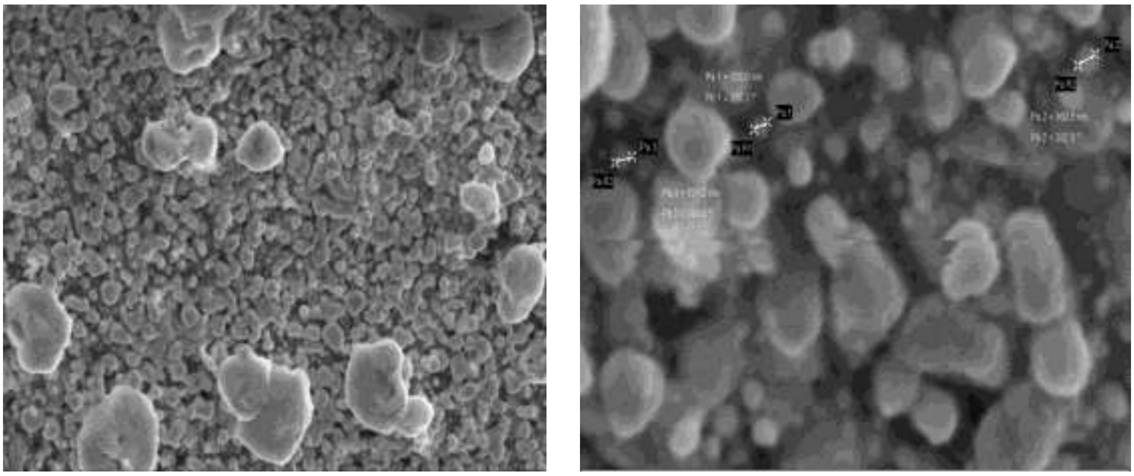

Figure 4: SEM images of Synthesized Mn-Ni-Zn nanoparticles

IV. CONCLUSION

In summary, for the first time, trimetallic (Mn-Ni-ZnNPs) alloy nanoparticles were successfully synthesized employing a simple, biocompatible, cost-effective, and non-hazardous method using the *Caparis zeylanica* plant extract. The synthesized trimetallic nanoparticle was verified using UV-visible and FT-IR spectroscopy. SEM analysis of trimetallic nanoparticles revealed that they were 128-169 nm in size and had a spherical shape.

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