

***Momordica charantia* as corrosion inhibitor and reductant for the green synthesis of gold nanoparticles**

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Abstract

Green chemistry which aims to reduce substances hazardous to human health and the environment in the design, development and implementation of chemical processes and product is becoming more and more important. In search for eco-friendly materials for the synthesis of metal nanoparticles and corrosion inhibition, the leaf-extract of *Momordica charantia* have identified, as it displays remarkable antioxidant property. The leaf-extract was investigated by weight-loss method in carbon steel to study the corrosion inhibition. The environmental friendly synthesis of nanoparticles process is a revolutionary step in the field of nanotechnology. In this study, the biosynthesis of gold nanoparticles was carried out using *M. charantia* leaf extract as reducing agent. UV-visible spectroscopy was used for quantification of gold nanoparticle synthesis. The formation of GNPs was rapid and within a few hours AuCl_4 was reduced into fine GNPs as evidenced by the appearance of deep ruby red colloidal dispersion. The UV-visible spectral analysis revealed the reduction of AuCl_4 and showed a peak at ~ 557 nm originating from the surface plasmon resonance of GNPs. The synthesized gold nanoparticles were characterized with scanning electron microscopy (SEM). The average size, geometrical shape and the zeta potential were discussed later.

Keywords: *Momordica charantia*, Corrosion inhibitor, Gold nanoparticles, SEM.

1. INTRODUCTION

Corrosion is defined as the deterioration of a metal due to its interaction with the environment. Due to corrosion many useful properties of metals such as malleability, ductility and electrical conductivity are compromised. Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty [1-5]. Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The field of nanotechnology is one of the most active areas of research in modern material sciences. Nanotechnology is a field that is

developing day by day, making an impact in all spheres of human life and creating a growing sense of excitement in the life sciences especially biomedical devices and biotechnology. Recently, the green chemistry which aims to reduce or eliminate substances hazardous to human health and the environment in the design, development and implementation of chemical processes and product is becoming more and more important. Many reports have been published in the literature on the biogenesis of gold nanoparticles using several plant extracts, particularly neem leaf broth (*Azadirachta indica*), alfaalfa (*Medicago sativa*), *Eucalyptus camaldulensis*, *Pelargonium roseum* [6,7].

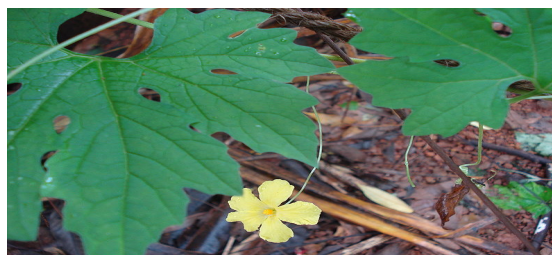


Figure - 1: *Momordica charantia* leaves.

In the present work was to investigate *Momordica charantia* leaves as a reductant for the synthesis of gold nanoparticle and as a corrosion inhibitor for carbon steel in ground water (Figure 1).

2. MATERIALS AND METHODS

2.1. Materials for green gold nanoparticles

Auric chloride hydrate was purchased from Sigma-Aldrich and de-ionised water was used for the preparation purpose. All the glass ware obtained from borosil and aqua regia was used for cleaning glassware as it can dissolve any residual metallic particles, which may interfere with the synthesis.

2.2. Collection of plant material

The *M. charantia* leaves were collected from Aranthangi, Pudukottai. The leaves were washed thoroughly 2–3 times with running tap water and the leaves are air dried under shade. After complete shade drying, the leaves were grinded in the mixer, the powder was kept in small plastic bags with proper labeling.

2.3. Methods

2.3.1. Preparation of extract

The dried leaves were thoroughly mixed with a methanol. The crude sample was extracted using percolation method. With this method the leaf material was moistened with methanol and repeatedly rinsed with methanol at regular intervals until all the active ingredients were collected. The crude was collected in a amber bottle and refrigerated [8].

2.3.2. Phyto chemical analysis

2.3.2.1. Preliminary phytochemical group test

The preliminary phytochemical group test of the methanol extract of dried leaves of *M. charantia* L. was performed by the standard methods [9–12].

2.3.3. Test for alkaloids

Small quantity of the methanol extract of dried leaves of *M. charantia* L. was treated with few drops of diluted hydrochloric acid, filtered and it was treated with Mayer's reagent and formation of yellowish buff colored precipitate indicated positive test for alkaloids.

The extract was treated with Dragendroff's reagent and the development of orange brown precipitate shows the presence of alkaloids.

2.3.4. Test for amino acids

Small amount of the methanol extract of dried leaves of *M. charantia* L. was dissolved in a few milliliters of distilled water and treated with

ninhydrin at the pH range of 4–8. The formation of purple color suggested the presence of amino acids.

2.3.5. Test for flavonoids

Small quantity of the methanol extract of dried leaves of *M. charantia* L. was dissolved in ethanol and was hydrolyzed with 10% sulphuric acid and cooled. Next, it was extracted with diethyl ether and divided into three portions in three separate test tubes.

One ml of diluted sodium carbonate solution, 1ml of 0.1M sodium hydroxide solution and 1ml of diluted ammonia solution were added to the first, second and third test tubes respectively. In each test tube, development of yellow color demonstrated the presence of flavonoids.

2.3.6. Test for steroids and triterpenoids

The presence of steroids and triterpenoids in methanol extract of dried leaves of *M. charantia* L. was confirmed through Libermann–Burchard reaction, by dissolving 10 mg of methanol extract of dried leaves of *M. charantia* L. in 1 ml of chloroform and 1 ml of acetic anhydride and add 1–2 ml of concentrated sulphuric acid slowly. A reddish violet ring at the junction of the two layers confirmed the presence of triterpenoids and steroids.

Salkowski test was utilized to confirm the presence of steroids. Concentrated sulphuric acid was added to the chloroform solution of methanol extract of dried leaves of *M. charantia* L., appearance of reddish-blue color in the chloroform layer and green fluorescence in acid layer, suggested the presence of steroids.

2.3.7. Test for reducing sugar

Aqueous solution of methanol extract of dried leaves of *M. charantia* L. was prepared by dissolving sufficient quantity of methanol extract of dried leaves of *M. charantia* L. in minimum amount of distilled water.

The aqueous solution of extract was filtered and Fehling's solution was added to the aqueous solution of extract in a test tube and heated for few minutes. Development of brick red color demonstrated the presence of reducing sugars.

2.3.8. Test for gums

The equal of volume of aqueous solution of extract and concentrated sulphuric acid were mixed and treated with Molish's reagent. Formation of red-violet ring at the junction of sulphuric acid layer and aqueous solution of

extract indicated the presence of gums (Molish's test).

2.3.9. Test for tannins

The aqueous solution of extract was treated separately with 10% aqueous potassium dichromate solution, 5% ferric chloride solution and 10% aqueous lead acetate solution. Development of yellowish brown precipitate, greenish black color and yellow color precipitate, respectively, demonstrated the presence of tannins.

2.3.10. Tests for saponins

Small quantity of methanol extract of dried leaves of *M. charantia* L. was dissolved in minimum amount of distilled water and shaken in a graduated cylinder for 15 minutes. Formation of stable foam suggested the presence of saponins.

2.4. Green synthesis of gold nanoparticles

2.5 ml of methanolic extract was mixed with 25 ml of 1mM chloroauric acid in 100 ml Beaker. The reaction mixture was kept aside in air dried oven for 15 minutes at 50°C. The color change from yellow to deep ruby-red indicated the formation of GNPs. The reaction mixture was centrifuged at 14,000 rpm for 15 min and the supernatant was discarded. The GNPs obtained as a pellet was dispersed in deionised water for further studies [13].

2.5. UV-visible spectroscopy

UV-visible spectrophotometer is the one of the important techniques for analysis of synthesized GNPs. After the synthesis, the pure GNPs were characterized by UV-visible absorption spectrophotometer (Systronics 119). The color change in reaction mixture (metal ion solution + plant extract) was recorded through visual observation. Synthesized GNPs was confirmed by sampling the absorption maxima was scanned by UV-visible spectrophotometer at the wavelength of 400–800 nm.

2.5.1. Scanning electron microscopy

The morphological characterization of the samples were done using vega3tescan (TESCAN ORSAY HOLDING, Czech Republic). In the SEM the electron beam is focused in to the affine probe and subsequently raster scanned over a small rectangular area. As the beam interacts with the sample it creates various signal (secondary electrons, internal currents and photon emission etc.) all of which can be probably detected.

2.5.2. Preparation of specimen

Carbon steel specimen (0.026% S, 0.06% P, 0.4% Mn and 0.1% C and rest Fe) of the dimensions 1.0 × 4.0 × 0.2 cm were polished to a

mirror finish and degreased with acetone and used for the weight-loss method and surface examination studies.

2.5.3. Weight-loss study

Carbon steel specimens in triplicate were immersed in 100 ml of the ground water containing various concentrations of the inhibitor in the presence and absence of inhibitor for 1 day¹¹. The weights of the specimens before and after immersion were determined using a ACCULAB Electronic top loading balance, with readability/sensitivity of 0.1 mg in 210 g range. Then the inhibition efficiency was calculated using the formula

$$IE = 100 [1 - (W2/W1)]\%$$

where W1 and W2 are corrosion rate in the absence and presence of inhibitor respectively.

The corrosion rate (CR) was calculated by using the formula

$$CR = [(weight\ loss\ in\ mg) / (area\ of\ the\ specimen\ in\ dm^2 \times immersion\ period\ in\ days)].$$

3. RESULTS AND DISCUSSION

The preliminary phytochemical group tests were performed by the standard protocol and the results are presented in Table 1. The results showed the presence of steroids, triterpenoids, alkaloids, flavanoids, tannins, amino acids, reducing sugar and saponins in methanol extract of *M. charantia* L. leaves [14].

Table – 1: Preliminary phytochemical group tests for the methanol extract of leaves *M. charantia* L.

Alkaloids	+
Steroids	+
Triterpenoids	+
Amino acids	+
Flavonoids	+
Gums	-
Reducing sugar	+
Tannins	+
Saponins	+
– Absence, + Presence	

3.1. Visual observation

Formation of gold nanoparticles was preliminarily well known by changing of yellow to ruby red colour while adding leaf extract with gold ion solution due to the excitation of free electrons in the nanoparticles [15]. The colour formation was occurs within a few min after addition of leaf

extract figure 2. Metal nanoparticles exhibits different colours in solution due to their optical properties. Gold nanoparticles were characterized by forming of ruby red colour. Previously, increasing colour intensity with in 30 min was observed using leaf extract of *Acalypha indica* [16].



Figure – 2: Colour change yellow to ruby red colour indicate the formation gold nanoparticles.

3.2. UV-visible spectra

The color change showed the presence of gold nanoparticles in the *M. charantia* leaf extract and it was characterized by UV-visible spectrophotometer and monitored by taking readings at in a Perkin Elmer (lambda25) UV-visible spectrophotometer. The strong broad peak located at 557nm was observed for gold nanoparticles (Figure 3).

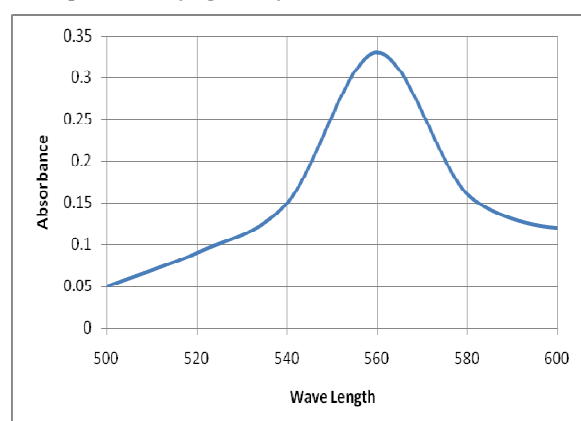


Figure – 3: UV spectrum of synthesis of gold nanoparticles.

3.3. Scanning electron microscope

The size, shape and distribution of green synthesized gold nanoparticles were characterized by scanning electron microscope (Figure 4). It shows particles are spherical with average size and also individual nanoparticles

were aggregated shows large nanoparticles. This aggregation took place due to the presence of cell components on the surface of nanoparticles and acts as capping agent. The SEM image of the AuNPs in sample confirmed that the particles are irregular spherical, hexagonal, triangular and elongated shapes [17].

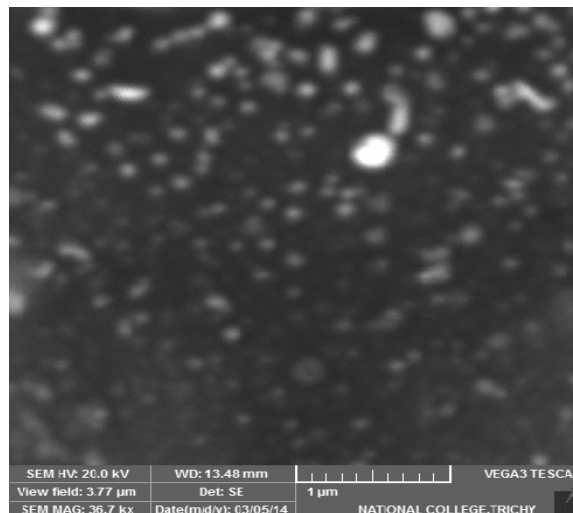


Figure – 4: SEM image of AuNPs

3.4. *Momordica charantia* as corrosion inhibitor

3.4.1. Analysis of results of weight-loss study

The weight loss studies were done in ground water in the presence and absence of various concentration of the leaves extract ranging from 10 to 800 ppm. Using the weight-loss data, the corrosion rate, inhibition efficiency and the optimum concentration of the extract have been calculated. From table 2, it was found that with the addition of the leaves extract, the weight-loss of the carbon steel decreased, and the corrosion rate also decreased. The optimum concentration of *M. charantia* was found to be 200 ppm with maximum inhibition efficiency of 96.78%.

3.4.2 Effect of pH on the IE of leaf extract

It is seen from (Table 3) that at pH 7, the extract *Momordica charantia* has 96.78 % IE. When pH is lowered to 1 by addition of dilute hydrochloric acid, the IE decreased to 64.46%. This is due to the fact that when the acid is added the protective film is broken by the aggressive H⁺ ion present in the acid. When the pH is increased to 11 by addition of diluted sodium hydroxide solution, the IE increased to 33 %. This is due to the fact that the phenolic-OH groups would have been ionized to phenolate anion, -O-Na⁺. This helped anchoring of phenolic O⁻ on the anodic sites of the metal surface However this 64.46% IE in acidic medium (pH 1) is lower than the IE of 96.78% in neutral medium.

Table - 2: Corrosion rates of carbon steel in ground water by weight-loss method

Concentration	Corrosion rate	Percentage inhibition
Blank	14.954	-
10	7.8593	47.44
50	9.2315	38.27
100	7.3603	50.78
200	0.4815	96.78
300	0.8733	94.16
400	0.6092	95.93
500	1.2184	91.85
600	3.4114	77.19
700	3.1676	78.82
800	4.7515	68.23

Table - 3: Corrosion rates of carbon steel in ground water due to the effect of pH on the IE of leaf extract

pH	Concentration	Corrosion rate	Percentage inhibition
1	Blank	294.862	64.46
	200	104.7905	
3	Blank	20.7710	44.14
	200	11.6018	
5	Blank	19.6482	12.57
	200	17.1784	
9	Blank	10.9649	13.33
	200	9.5029	
11	Blank	18.2749	33.00
	200	12.2442	

4. CONCLUSION

Biological synthesis of nanoparticle has upsurge in the field of nano-biotechnology to create novel materials that are eco-friendly, cost effective, stable nanoparticles with a great importance in the areas of electronics, agriculture and medicine.

- The rapid synthesis of gold nanoparticles using *Momordica charantia* extract has been demonstrated.
- The reduction of gold nanoparticles takes place because of the presence of anti oxidant property in the *Momordica charantia* leaf extract.

- The uv-visible spectra measurements were carried out at 557 nm with absorption peak.
- The surface morphology of the nanoparticle was observed from the SEM analysis.
- The *Momordica charantia* leaf was also act as corrosion inhibitor for carbon steel in ground water medium with inhibition efficiency 96.78 %

Acknowledgments

Thanks for Holy Cross College (Autonomous), Tiruchirappalli management.

5. REFERENCES

1. Kumar CSSR, Srinivas M and Yakkundi S. Limonoides from the seeds of *Azadirachta indica*. **Phytochemistry**, 1996; 43: 451.
2. Schaaf O, Jarvis AP, van der Esch SA, Giagnacovo G and Oldham NJ. Rapid and sensitive analysis of azadirachtin and related triterpenoids from Neem (*Azadirachta indica*) by high-performance liquid chromatography-atmospheric pressure chemical ionization mass spectrometry. **Journal of Chromatography A**, 2000; 886: 89.
3. Khuzhaeu VU and Aripova SF. Pseudocarpaine from *Carica papaya*. **Chemistry of Natural Compounds**, 2000; 36: 418.
4. Okafor PC and Ebenso EE. Inhibitive action of *Carica papaya* extracts on the corrosion of mild steel in acidic media and their adsorption characteristics. **Pigment and Resin Technology**, 2000; 36: 134.
5. Okafor PC, Ikpi ME, Uwah IE, Ebenso EE, Ekpe UJ and Umoren SA. Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media. **Corrosion Science**, 2008; 50: 2310.
6. Kalimuthu K, Venkataraman D, SureshBabu RKP, Muniasamy K, Selvaraj BM, Bose K and Sangiliyandi G. Biosynthesis of silver and gold nanoparticles using *Brevibacterium casei*. **Colloids and Surfaces B: Biointerfaces**, 2010; 77: 257-262. (doi:10.1016/j.colsurfb.2010.02.007).
7. Geddes CD, Parfenov A, Gryczynski I and Lakowicz JR. Luminescent blinking of gold nanoparticles. **Chemical Physics Letters**, 2003; 380: 269-272. (doi:10.1016/j.cplett.2003.07.029).
8. Zubair M, Rizwan K, Rasool N, Afshan N, Shahid M and Ahmed V. Antimicrobial potential of various extract and fractions of leaves of *Solanum nigrum*. **International**

- Journal of Phytomedicine**, 2011; 3(1): 63–67.
9. Tyler VE, Brady LR and Robbers JE. Pharmacognosy, 9th Ed., **Lea and Febiger, Philadelphia**. 1993.
 10. Pollock JRA and Stevens R. Editors. Dictionary of organic compounds, 4th Ed., **Eyre and Spottiswoode, London**. 1965.
 11. Trease GE and Evans WC. Pharmacognosy, 12th Ed., **ELBS Publication, East Bourne**. 1996.
 12. Plummer DI. An introduction to practical biochemistry, 2nd Ed., **Tata Macgraw-Hill Publishing, New Delhi**. 1985.
 13. Phong NTP, Minh NH, Quoc HC and Quoc V. Green synthesis of gold nanoparticle colloidal solutions and used as a new X-ray contrast agent. **University of Sciences, VNU HCM City**.
 14. Ganesan A, Natesan S, Perumal PG, Vellayutham R, Manickam K and Ramasamy N. Iranian Journal of Pharmacology & Therapeutics. 2008; 7: 43–47.
 15. Safaepour M, Shahverdi AR, Shahverdi HR, Khorramizadeh MR and Gohari AR. Green synthesis of small silver nanoparticles using geraniol and its cytotoxicity against Fibrosarcoma-Wehi 164. **Avicenna Journal of Medical Biotechnology**, 2009; 2: 111–115.
 16. Krishnaraj C, Jagan EG, Rajasekar S, Selvakumar P, Kalaichelvan PT and Mohan N. Synthesis of silver nanoparticles using *Acalypha indica* leaf extracts and its antibacterial activity against water borne pathogens. **Colloids and Surfaces B: Biointerfaces**, 2010; 76(1): 50–56.
 17. Boruah SK, Boruah PK, Sarma P, Medhi C and Medhi OK. Green synthesis of gold nanoparticles using *Camellia sinensis* and kinetics of the reaction. **Advanced Materials Letters**, 2012; 3(6): 481–486.