World Journal of Nano Science & Technology 3(2): 59-65, 2014
ISSN XXXX-XXXX

DOI: 10.5829/idosi.wjnst.2014.3.2.113

Green Synthesis of Gold Nanoparticles Using Cucumis Sativus (Cucumber) Aqueous Extract

[1]*Monalisa Pattanayak,* [2]*T. Muralikrishna and* [1]*P.L. Nayak*

[1]P.L. Nayak Research Foundation and Centre for Excellence in Nano Science and Technology,
Synergy Institute of Technology, Bhubaneswar, Odisha, India
[2]Jawaharlal Nehru Technological University, Kakinada, Andhra Pradesh, 533003, India

Abstract: In the present study we explore the reducing and capping potential of aqueous extract from juice of cucumber for the synthesis of gold nanoparticles. The extract with different concentration reduced with $HAuCl_4$ aqueous solution at room temperature. The color change, pH change and UV-visible spectroscopic analysis reveal the Surface Plasmon Resonance (SPR) of the final reaction product which confirms the reduction of Au^{3+} ion to gold nanoparticles. XRD, particle size analysis results represent strong reducing potential of cucumber aqueous extract which can also be tested in the green synthesis of other metallic nanoparticles.

Key words: Aqueous extract · Gold nanoparticles · Surface Plasmon Resonance (SPR) · Capping · Cucumber

INTRODUCTION

In the last few years the field of nanobiotechnology has received immense attention due to its vast applicability from the kitchen to space. With this development, many new ecofriendly methods for the synthesis of nanoparticles have emerged viz. plant mediated synthesis, microorganism mediated synthesis etc, in order to minimise the risk of pollut ion to environment and toxicity associated with the use of reductive chemicals in the nanoparticles synthesis. For the development of green chemistry, Raveendran *et al*. suggested that three main factors in nanoparticle preparation should be considered i.e. solvent choice, the use of an environmentally benign reducing agent, and the use of a non-toxic material for nanoparticle stabilisatio [1]. In this respect, plant mediated synthesis of nanoparticles is not only ecofriendly, cheap and safe to handle but the many bio chemicals from the plant posses vast therapeutic potential, which could be employed to alleviate the sufferings of humanity through a suitable drug delievery technique. Metallic gold nanoparticles have tremendous applications in cancer diagnosis & therapy, catalysis and in optoelectronics. For e.g. Goldnanoparticle solutions are bright red/purple colored due to plasmon absorption. Any surface modification of AuNPs results in the shift of plasmon absorption wavelength. This change in optical property of AuNPs when coming in contact with the probe biomolecules is exploited to develop biosensors [2]. Hainfeldetal. demonstrated that the irradiation of AuNPs accumulated in tumor with 250 kVp X-rays caused shrinkage of tumor in mice with subcutaneously grown mammary carcinoma tumor. It was also found that that treatment with X-rays alone had no therapeutic effect on the tumor [3]. Recently a lot of work has been done with regard to plant mediated synthesis of metallic nanoparticles. Cucumber (Cucumis sativus) is a widely cultivated plant in the gourd family Cucurbitaceae. It is a creeping vine that bears cylindrical fruits that are used as culinary vegetables. There are three main varieties of cucumber: slicing, pickling, and burpless. Within these varieties, several different cultivars have emerged. The cucumber is originally from Southern Asia, but now grows on most continents. Many different varieties are traded on the global market. The cucumber is a creeping vine that roots in the ground and grows up trellises or other supporting frames, wrapping around supports with thin, spiraling

Corresponding Author: Monalisa Pattanayak, P.L. Nayak Research Foundation and Centre for Excellence in Nano Science and Technology, Synergy Institute of Technology, Bhubaneswar, Odisha, India.

tendrils. The plant has large leaves that form a canopy over the fruit. The fruit of the cucumber is roughly cylindrical, elongated with tapered ends, and may be as large as 60 centimeters (24 in) long and 10 centimeters (3.9 in) in diameter. Having an enclosed seed and developing from a flower, botanically speaking, cucumbers are classified as accessory fruits. Much like tomatoes and squash they are often also perceived, prepared and eaten as vegetables. Cucumbers are usually more than 90% water.

Gold Nanoparticles: Elemental gold has many unique properties which have attracted and fascinated mankind since its discovery. Being very unreactive, gold does not turnish in the atmosphere and so keeps its attractive colour forever [4]. That is one of the main reasons why gold has been used in shaping jewelleries. It has been used for many colourful, decorative, ceremonial and religious artifacts and has been a metal with a high monetary value. Colourful aqueous solutions of gold colloids date back to Roman times and were known to medieval alchemists as aurum potabile [5]. A Roman cup, called the Lycurgus cup, used nanosized (ca 50 nm) gold and silver alloys, with some Cu clusters to create different colours depending on whether it was illuminated from the front or the back. The cause of this effect was not known to those who exploited it. Michael Faraday was the first to recognise that the colour was due to the minute size of the gold particles [6]. On February 5, 1857, Michael Faraday delivered the Bakerian Lecture of the Royal Society in London entitled "Experimental Relations of Gold (and other metals) to Light". In his speech, he mentioned that known phenomena (the nature of the ruby glass) appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colours. Nearly a century later, electron microscope investigations on Faraday's rubycoloured gold colloids have revealed that Faraday's fluid preparations contain particles of gold of average diameter (6±2 nm) [7]. Although some scientists see the Faraday's experiment as a landmark in the history of nanoscience and nanotechnology [8] the chemical inertness of gold as a bulk metal appeared to provide very little opportunities to open up new and exciting chemistries (Hutchings *et al*., 2008). The new field of nanotechnology made it possible to discover the unique properties of matter when subdivided to the nanoscale. Gold at nanoscale manifests a number of interesting physico-chemical properties that have fascinated many disciplines of science including: material scientists, catalysts, biologists, surface and synthetic chemists and theoreticians in great number. Today, in the 21st century, gold chemistry is based on solid ground regarding the preparation and characterisation of a wide variety of fundamental compounds with gold atoms and gold clusters as core units [9-11]. The fact that gold NPs have been studied in many different scientific fields has led not only to a deep understanding of many of the physico-chemical features that determine the characteristic behaviour of these nanoscale gold nanoaprticles but also to invent, test and validate reliable novel procedures for the preparation, synthesis and characterisation of gold nanoparticles of basically any desired size and shape.

The bottom up process by far more common and effective [12] and has become a popular method in current nano-science and nanoengineering. It has a number of potentially very attractive advantages. These include experimental simplicity down to the atomic size scale, the possibility of three-dimensional assembly and the potential for inexpensive mass fabrication [13]. The simplest and most common bottom up method employed for the production of the gold nanoparticles of different sizes is the reduction of Au (III) salt (usually $HAuCl_4$) by sodium citrate in water. In this method, pioneered by Turkevich and co-workers in 1951(Turkevich, 1951) and later refined by Frens in the 1970s [14] and more recently further developed by Kumar [15]. It is generally accepted that the $AuCl_4^-$ ions are first reduced to atomic gold (Au), the concentration of which rises quickly to the supersaturation level. Collision of the Au atoms leads to a sudden burst of nuclei formation which marks the start of the nucleation step. It is the attachment and coalescence of those nuclei which results in the growth and formation of desired nanoparticles [16]. Figure 1 illustrates the reduction, nucleation and growth steps during the formation of the nanoparticles. It shows that the reduction and nucleation are fast (>200 ms) while growth step is the rate determining step since it is much slower than the antecedent nucleation step. Many times, difficulty in controlling the nucleation and growth steps, which are intermediate stages of particle formation process may result in a broad particles size distribution [17]. In the presence of various reactive polymers in the reaction medium, that is, polymers having various functional groups, the growing metallic particles are stabilized by the adsorption of the polymer chains onto the surface of the growing metal fragments, thus lowering their surface energy and creating a barrier to further aggregation [18].

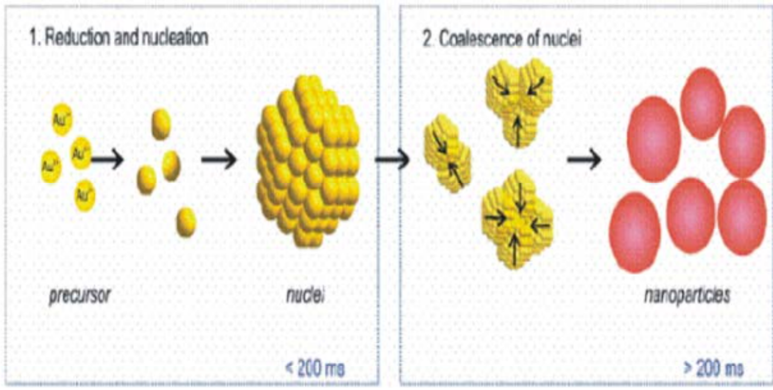


Fig. 1: Schematic illustration for the deduced process of gold nanoaparticles formation. Reduction and nudeation are faster processes than coalescence of nuclei (Polte *et al*., 2010) Reprinted with the permission from copyright 2010 American chemical society

One important factor for understanding the behaviour of the natural particles in the environment and the bioavailability of heavy metals loaded on them is their interaction with microorganisms associated with biomass population. The nanoparticles could possibly be immobilised, absorbed, reacted or retarded by biomass in the environment.

MATERIAL AND METHOD

Reagents and Chemicals: Tetrachloroauric acid ($HAuCl_4$•XH_2O) was obtained from Sigma Aldrich Chemicals. Freshly prepared triple distilled water was used throughout the experimental work [19-47].

Preparation of Cucumber Aqueous Extract: In our synthesis procedure, cucumber aqueous extract were used as reducing and capping agent. Extract was prepared by soaking 2 gm of cucumber in 20 ml deionized water for overnight and crush it with mortar and pastle, the mixture was boiled for 10-15 minute at 70-80°C. The extract was followed by centrifuge for 15 minute at 5000 rpm; collected supernatant was then filtered by standard sterilized filtration method. Extract was then stored at 4°C for further use.

Synthesis of Gold Nanoparticles: In a typical experiment, AuNPs synthesis protocol was optimized by stirring a mixture of cucumber aqueous extract at three different concentrations with 1mM $HauCl_4$ aqueous solution (1;1, 5;1, 10;1) at 200 rpm at room temperature for 1 hour. Within a particular time change in color was observed indicating nanoparticle synthesized.

Table 1: Indication of Colour change in green synthesis of Gold nanoparticles

Nanoparticle Solution	Colour change Before	After	Colour intensity	Time
Cucumber	Off White	Golden Brown	+++	24 Hours

Table 2: Indication of change in P^H during green synthesis of Gold nano particles

Nanoparticle Solution	P^H change Before Reduction	After Reduction	Result
Cucumber	6.41	1.08	+

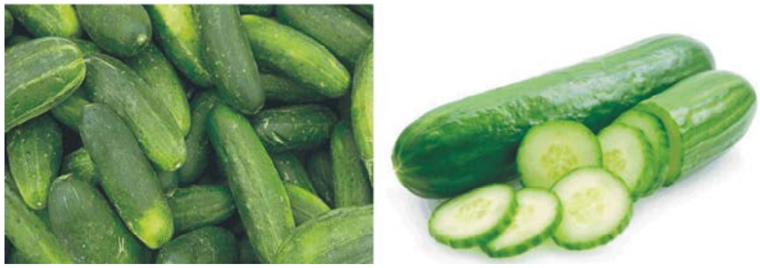
UV-VIS Spectra Analysis: The reduction of pure Au^{3+} to nanoparticle was monitored by measuring the UV-vis spectrum the most confirmatory tool for the detection of surface Plasmon resonance property (SPR) of AuNPs, by diluting a small aliquot of the sample in distilled water. UV- Vis spectral analysis was done by using UV-Vis spectrophotometer Systronics 118 within the range of 350-650 nm.

X-ray Diffraction (XRD) Analysis: XRD measurement of biologically synthesized AuNPs from tertrachloroauric acid, AuNPs solution drop-coated on glass were done on a Bruker axs- D8 Advance instrument operating at a voltage of 40 KV and current of 20 mA with Cu Kα radiation.

Particle Size Analysis: Size analysis of gold nanoparticles were carried out on Brookhaven 90 Plus Nanoparticle Size Analyzer with following measurement parameter, Refractive index fluid-1.330, Angle-15.00, Average count rate-5.2kcps with run completed 3 times.

RESULTS AND DISCUSSION

Image of Cucumber shown below:



Cucumber Vegetable

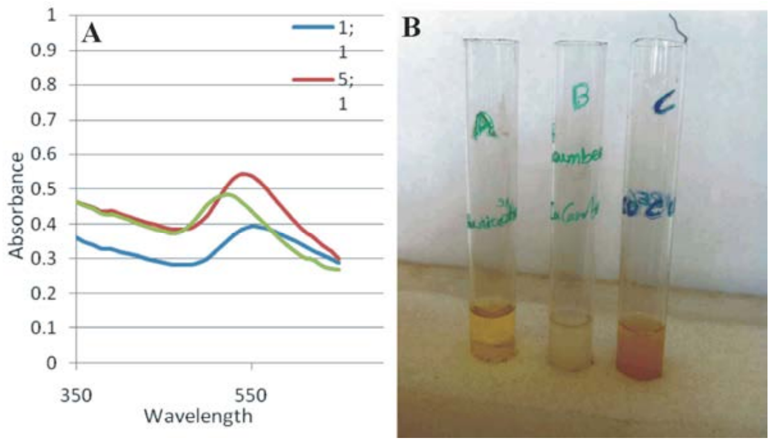


Fig. 2: A UV-Vis spectra of AuNPs synthesized by reacting different concentration of Cucumis Sativus extract with 1mM $HAuCl^4$ aqueous solution (5;1, 10;1, 1;1) at room temperature. **B** Tube A- contains yellow color gold solution, Tube B- contains Off white color Cucumis Sativus extract, Tube C- contains Golden Brown color gold nanoparticles solution.

UV-VIS Spectroscopic Analysis of Au Nanoparticles: The appearance of violet color evident that the formation gold nanoparticles in the reaction mixture and the efficient reduction of the Au^{3+} to Au^0 (Fig.2B), the formed color solution allowed to measure the absorbance against distinct wave length to conform the formation of gold nanoparticles. The corresponding UV-vis absorption spectra are shown in Fig. 2A. The change in pH of aqueous gold solution 2.95 and cucumber extract 6.41 to 1.08 of cucumber gold nanoparticles solution in 1hour. In the present work, AuNPs synthesis with three different concentration of cucumber extract with fixed concentration of gold solution as ratio 1; 1, 5; 1, 10; 1. UV-vis scanning of reaction product showed SPR absorption band and peaks (Fig. 2a). Reaction mixture with 1;1 ratio, in which reduction of Au^{3+} ions just to occurred and SPR band intensities was less and peak is broad which suggest partial reduction of Au^{3+} ion and formation of larger AuNPs with SPR at 550 nm. And in reaction mixture ratio 1;10 the observed intensity of SPR peak is more with small sharpness in the peak compare to the reaction mixture 1;1 with SPR at 530 nm. Where as in reaction mixture 1; 5 the SPR band intensity and peak is highest indicating complete reduction of gold ions with SPR at 540 nm. Thus maximum yield of reduced sized AuNPs at reaction ratio 5; 1 suggested as optimum reaction condition under room temperature condition.

XRD Analysis: The crystalline structure of biologically synthesized AuNPs using cucumber extract were analyzed by XRD measurements. A typical XRD pattern of the Au was found by Bragg reflections corresponding to (111), (200) and (220) sets of lattice planes are observed that may be indexed on the bases of the fcc structure of gold. The characteristic peaks corresponding to (111), (200) and (220) are located at 2θ= 38.80°, 44.13° and 64.82°

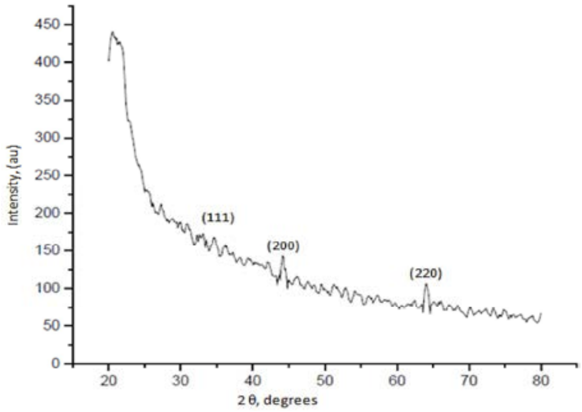


Fig. 3: XRD of gold nanoparticles.

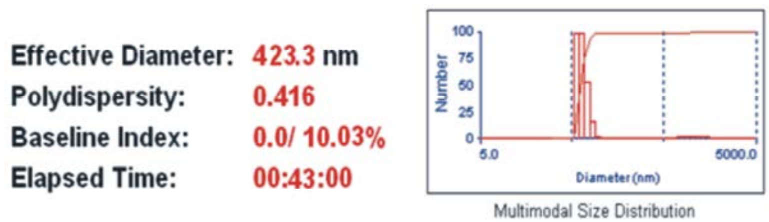


Fig. 4: Particle size analysis.

respectively and the weak intensities of peaks indicates that gold nanocrystals are embedded in the film, shown in Figure 3.

Particle Size Analysis: Laser diffraction particle size analyzer provides the detail about the particle nature, such as monodispersed, didispersed and polydispersed. Our investigation revealed that nanoparticles show polydispersity at 0.416 indexing and various sizes of nanoparticles ranging with effective diameter around 423.3 nanometer, lognormal summary given below in Figure 4.

CONCLUSION

The study demonstrates the rapid synthesis of gold nanoparticles with small sized and high crystallinty. The reduction of the metal ions and stabilization of the gold nanoparticles is believed to occur by the proton releasing hydroxyl group , containing α-terpineol, citronellol, borneol, trans-nerolidol, cis/trans-linalol oxides, ã-sitosterol, phytol, geraniol, stigma sterol or any other secondary metabolites and various acids present in extract. The concentration of cucumber extract and metal ions plays a crucial role for the synthesis of gold nanoparticles of desired size with reaction conditions. The spectroscopic characterizations using UV-vis, XRD, and Particle size analysis were useful in providing the formation of nanoparticles and also to confirm their characteristic. From literature study proposed that hydroxyl and amine group containing components are responsible as an active reductant and capping agent, but further FTIR analysis can give evidence to understand the appropriate chemical and molecular interactions which could be responsible for the gold salt reduction. As, the appearance of single peak in UV-Vis spectrum represents spherical shape of generated nanoparticles which can be further confirmed by representing the Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) images.

REFERENCES

1. Raveendran, P., J. Fu and S.L. Wallen, 2003. Completely "green" synthesis and stabilization of metal nanoparticles, J. Am. Chem. Soc., 125(46): 13940-13941.
2. Katz, E. and I. Willner, 2004. Integrated nanoparticle-biomolecules hybrid systems: Synthesis, properties, and applications. Angew Chem Int, 43(45): 6042.
3. Hainfeld, J.F., N.S. Daniel and M.S. Henry, 2004. The use of gold nanoparticles to enhance radiotherapy in mice, Physics in med and Bio, 49(18): 309.
4. Hutchings, G.J., M. Brust and H. Schmidbaur, 2008. Gold -an introductory perspective,Chemical Society Reviews, 37: 1759-1765.

5. Mellor, J.W., 1923. A Comprehensive Treasise on inorganic and Theoretical Chemistry, London, Longmans, Green and Co.
6. Faraday, M., 1857. The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light. Philosophical Transactions of the Royal Society of London, 147: 145-181.
7. Turkevich, P.C.S. and J. Hiller, 1951. A study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold, Discussions of the Faraday Society, 11: 55-75.
8. Peter, P.E. and T. John Meurig, 2007. Gold in a Metallic Divided State-From Faraday to Present-Day Nanoscience, Angewandte Chemie, International Edition, 46: 5480-5486.
9. Murray, H.H., 2000. Gold: Progress in Chemistry, Biochemistry and Technology Edited by Hubert Schmidbaur (Technical University of Munich, Germany). John Wiley & Sons: New York. 1999. ISBN 0-471-97369-6, Journal of the American Chemical Society, 122: 4534-4534.
10. Peter, J.S., 2000. Gold-Progress in Chemistry, Biochemistry and Technology. H. Schmidbaur (ed.) John Wiley & Sons, Chichester, 1999 ISBN 0-471-97369-6, Applied Organometallic Chemistry, 14: 171.
11. Gagotsi, Y., 2006. Nanomaterials Handbook, Newyork, Taylor & Francis Group.
12. Sardar, R., A.M. Funston, P. Mulvaney and R.W. Murray, 2009. Gold Nanoparticles: Past, Present, and Futureâ Langmuir, 25: 13840-13851.
13. Brust, M. and C.J. Kiely, 2002. Some recent advances in nanostructure preparation from gold and silver particles: a short topical review. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 202: 175-186.
14. Frens, G., 1973. Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. Nature Phys. Sci., 241: 20-22.
15. Kumar, S., K.S. Gandhi and R. Kumar, 2006. Modeling of Formation of Gold Nanoparticles by Citrate Method, Industrial & Engineering Chemistry Research, 46: 3128-3136.
16. Pong, B.K., H.I. Elim, J.X. Chong, J.I.W. Trout and B.L. Lee, 2007. New Insights on the Nanoparticle Growth Mechanism in the Citrate Reduction of Gold (III) Salt: Formation of the Au Nanowire Intermediate and Its Nonlinear Optical Properties. The Journal of Physical Chemistry C, 111: 6281-6287.
17. Bellloni, J., 1996. Metal Nanocolloids. Current Opinion in Colloid & Interface Science, 1: 184-196.
18. King, S., K. Hyunh and R. Tannenbaum, 2003. Kinetics of Nucleation, Growth, and Stabilization of Cobalt Oxide Nanoclusters,The Journal of Physical Chemistry B, 107: 12097-12104.
19. Pattanayak Monalisa, and PL Nayak , 2012. Ecofriendly Green Synthesis of Iron Nanoparticles from Various Plants and Spices Extract, International Journal of Plant, Animal and Environmental Sciences, 1: 68-78.
20. Pattanayak Monalisa and PL Nayak, 2013. Natural Based Polysaccarides for Control Drug Release, International Journal of Research and Reviews in Pharmacy and Applied Science, 1: 72-117.
21. Pattanayak Monalisa, and PL Nayak, 2013. Green Synthesis of Gold Nanoparticles Using Elettaria cardamomum (ELAICHI) Aqueous Extract. World Journal of Nano Science & Technology, 1: 1-5.
22. Pattanayak Monalisa, and P.L. Nayak, 2013. Green Synthesis and Characterization of Zero Valent Iron Nanoparticles from the Leaf Extract of Azadirachta indica (Neem), World Journal of Nano Science & Technology, 106: 09.
23. Parida, U.K., B.K. Bindhani and P.L. Nayak, 2011. Green Synthesis and Characterization of Gold Nanoparticles Using Onion (Allium cepa) Extract. World Journal of Nano Science and Engineering, 1: 93-98.
24. Lal, S.S. and P.L. Nayak, 2012. Green synthesis of Gold Nanoparticles Using Various Plants and Spices Extract, International Journal of Science Innovation and Discovery, 2: 2.
25. Willets K.A.V. and R.P. Duyne, 2007. Localized surface Plasmon resonance spectroscopy and sensing. Anu Rev Phys Chem, 58: 267-297.
26. Kreibig, U. and M. Vollmer, 1995. Optical Properties of Metal Clusters. New York: Springer.
27. Sayeed, El, 2001. M. A. Some Interesting Properties of Metal Confined in Time and Nanometer Space of Different Shapes Acc Chem Res., 34: 4-257.
28. Narayanan, R. and El-Sayed, 2003. MA Effect of Catalytic Activity on the Metallic Nanoparticle Size Distribution:? Electron-Transfer Reaction between Fe $(CN)_6$ and Thiosulfate Ions Catalyzed by PVP-Platinum Nanoparticles, J. Phys. Chem. B, 107: 12416.
29. Narayanan, R. and El-Sayed, 2003. M.A.J. Am. Chem. Soc., 125: 8340.
30. Esumi, K., A. Kameo, A. Suzuki and K. Torigoe, 2001. Preparation of gold nanoparticles in formamide and N, N-dimethylformamide in the presence of poly (amidoamine) dendrimers with surface methyl ester groups, Colloids Surf, A Physicochemical Eng Asp, 189: 155-61.

31. Feitz, A., J. Guan and D. Waite, 2006. Process for producing a nanoscale zerovalent metal, US Patent Application Publication, US2006/ 0083924 A1.
32. Lovely, D.R., J.F. Stoltz, G.L. Nord and E.J.P. Phillips, 1987. Anaerobic production of magnetite by a dissimilatory iron-reducing microorganisms., Nature, 330: 252-254.
33. Mohanty, L., U.K. Parida, A.K. Ojha and P.L. Nayak, 2011. J of Micro and Antimicro, pp: 3.
34. Song, J.Y. and B.S. Kim, 2010. Rapid biological synthesis of silver nanoparticles using plant leaf extracts, Bioprocess Biosyst Eng., 33: 79-84.
35. Song, J.Y., E.Y. Kwan and B.S. Kim, XXXX. Biological synthesis of platinium nanoparticles using Diopyrus kaki leaf extract, Bioprocess Biosyst Eng., 33: 159-164.
36. Das, R.K., B.B. Borthakur and U. Bora, 2010. Green synthesis of gold nanoparticles using ethanolic leaf extract of Centella asiatica. Mat Lett, 64: 1445-1447.
37. Nune, S.K., N. Chanda, R. Sukhla, K. Katti, R.R. Kulkarni, S. Thilakavathy, S. Mekapothula, R. Khanna and K.V. Katti, 2009. Green nanotechnology from tea: Phytochemicals in tea as building blocks for production of biocompatible gold nanoparticles, J. Mat Chem, 19: 2912-2920.
38. Smithaa, S.L., D. Philip and K.G. Gopchandrana, 2009. Green synthesis of gold nanoparticle using Cinnamomum zeylanicum leaf broth. Spectrochim Acta PartA, 74: 735-739.
39. Agnihotri, M., S. Joshi, A.R. Kumar, S. Zinjarde and S. Kulkarni, 2009. Biosynthesis of gold nanoparticles by the tropical marine yeast Yarrowia lipolytica NCIM 3589 Mat Lett, 63: 1231-1234.
40. Philip, D., 2009. Biosynthesis of Au, Ag and Au-Ag nanoparticles using edible mushroom extract. Spectrochimica Acta Part A, 73: 374-381.
41. Trease & Evans, Pharmacogonosy. W.B Sounders, 15 Edition, pp: 353-354.
42. Shaban, M.A.E., K.M. Kandeel, G.A. Yacout and S.E. Mehase, XXXX. The chemical composition of the volatile oil of Elettaria cardamomum seeds Pharmazie, 42: 207-208.
43. Noleau, I., B. Toulemonde and H. Richard, XXXX. Voatile constituents of cardamom ElettariaD cardamomum Maton cultivated in Costa Rica, Flavours Frag J., 2: 123-127.
44. Gopalakrishnan, M., C.S. Narayanan and M. Grenz, XXXX. Non saponifiable lipid constituents of cardamom, J. Agri Food Chem, 38: 2133-2136.
45. Duke, J.A., XXXX. Handbook of Phytochemical Constituents of GRAS Herbs and others Economic Plants: Herbal reference library, CRC Press, London, pp: 239-240.
46. Starnes Daniel Lee, 2009. In Planta “Green Engineering” of variable sizes and exotic shapes of Gold Nanoparticles: An Integrative Eco-friendly Approach. PhD Thesis, pp: 3-5.
47. Singh, A.K., M. Talat, D.P. Singh and O.N. Srivastava, 2010. Biosynthesis of gold and silver nanoparticles by natural precursor clove and their functionalization with amine group, Journal of Nanopart Research, 12: 1667-1675.