

Green Synthesis, Spectral Characterization, Particle Image and Size Analysis of Silver Oxide Nanoparticles Mediated by Extract of Orange (*Citrus sinensis*) waste peel

K. Priyadharshini¹, Dr. K. Sathiyamoorthi², Dr. S. Velmurugan^{3&4*}

PG Students, PG & Research Department of Physics, Government Arts College, Chidambaram¹

Assistant Professor, PG & Research Department of chemistry, Government Arts College, Chidambaram².

PG & Research Department of Physics, Government Arts College, Chidambaram Tamil Nadu, India^{3*}

Department of Physics Annamali University, Annamalainagar, Chidambaram^{4*}

drvelmuruganphy@gmail.com

Abstract: A novel approach for the utilization of Orange fruit waste is attempted in the present investigation. Orange (*Citrus sinensis*) fruit seed aqueous extract was utilized for green synthesis of silver oxide nanoparticles (AgONPs). The phytoconstituents in the seed acted as reducing and stabilizing agent for AgONPs formation. UV-Vis, FT-IR, FL, XRD, DLS and SEM, analysis were used to characterize the green synthesized AgONPs. DLS and SEM confirmed the crystalline nature. FT-IR revealed functional groups like alcohol or phenols, carboxylic acids, ketones, amines, aromatic amines, aliphatic amines, alkyl halides and alkynes which were responsible for AgONP formation. The nanoparticles showed more CV study of silver oxide nanoparticle. OrangeFruit waste can be successfully utilized for seriumnano particles formation which can be therapeutically useful and effective.

Keywords: Green synthesis, AgONPs, Orange (*Citrus sinensis*), UV-Vis, FT-IR, FL, XRD, DLS and SEM and CV study

I. INTRODUCTION

Nanotechnology is a science, dealing with the synthesis of nanoscale materials (range in size from 1 to 100 nm) [1-2], and their applications. The metallic nanoparticles have various categories including gold, silver alloy, zinc and others [3-5]. Silver nanoparticles have considerable attention among metal nanomaterials, due to their physicochemical properties [6]. They are in great demand due to their widespread applications e.g., antimicrobials and therapeutics, bimolecular detection, biolabeling, catalysis and microelectronics, nonlinear optics and intercalation materials for electrical batteries [7-8]. Biological synthesis of metal nanoparticles has been well achieved by different microorganisms. Actinomycetes are considered an important resource for new products of medical and industrial interest such as antimicrobial agents [9]. They are being used as eco-friendly nanofactories [10-11]. Actinomycetes are efficient candidates for metal nanoparticles production extracellularly and intracellularly. The synthesis of nanoparticles by actinomycetes represents good stability and polydispersity. Actinomycetes possess important biocidal activity against different pathogens [12]. Moreover, it can be manipulated genetically in order to provide better control over size. Optimization of the growth conditions, such as media components, pH, temperature, substrate concentration and inoculum size will not only support the growth but also enhance the productivity and monitor the rate of enzyme activity which affects the synthesis of silver nanoparticles [13]. Statistical experimental designs depend on many steps of an optimization strategy, such as searching for optimal conditions of the targeted factor or for screening experiments [14]. Plackett–Burman design is one of the popular and economic choices for bio-processing [15-16]. Silver nanoparticles are nanoparticles of silver of between 1 nm and 100 nm in size [17]. While frequently described as being 'silver' some are composed of a large percentage of silver oxide due to their large ratio of surface-to-bulk silver atoms. Numerous shapes of nanoparticles can be constructed depending on the application at hand. Commonly used are spherical silver nanoparticles but diamond, octagonal and thin sheets are also popular. Their extremely large surface

area permits the coordination of a vast number of ligands.. When the concentration increases enough, dissolved metallic silver ions bind together to form a stable surface. The surface is energetically unfavorable when the cluster is small, because the energy gained by decreasing the concentration of dissolved particles is not as high as the energy lost from creating a new surface [18]. When the cluster reaches a certain size, known as the critical radius, it becomes energetically favorable, and thus stable enough to continue to grow. This nucleus then remains in the system and grows as more silver atoms diffuse through the solution and attach to the surface[19-20] When the dissolved concentration of atomic silver decreases enough, it is no longer possible for enough atoms to bind together to form a stable nucleus. At this nucleation threshold, new nanoparticles stop being formed, and the remaining dissolved silver is absorbed by diffusion into the growing nanoparticles in the solution.

II. MATERIAL AND METHODS

2.1. Collection of Sample

The Orange (*Citrus sinensis*) fruit (Figure:1) purchased from fruit stall in Chidambaram town, the purchased fruits after eaten peels are through to the dust pin. I was collect that waste peels, washed thrice in the running tap water, then sliced in small pieces, the pieces are dried in seven days in sun light, the dried peels were grained to powder. The powdered Orange (*Citrus sinensis*) fruit peels stored and further green synthesis process.

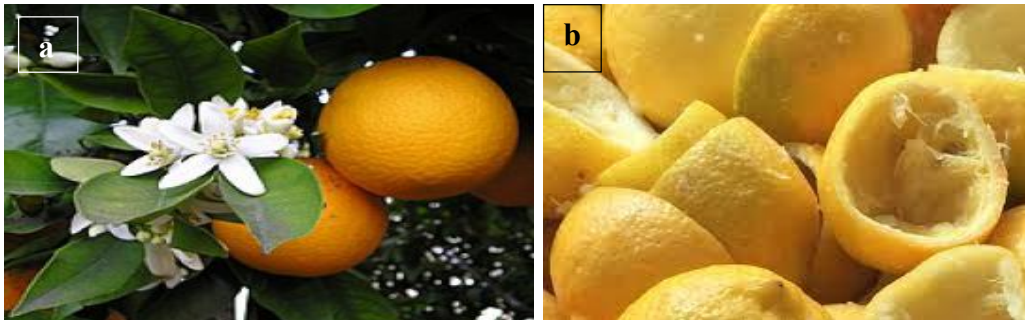


Figure: 1 (a) Orange fruit with their plant, (b) Waste peel of Orange fruits.

2.2. Chemicals, Solvents and Starting Materials

De-ionized water, whatmann 1 μ and whatmann 41 μ filter papers, Potassium di chromate Ethyl alcohol, sodium hydroxide pellets, Hydrochloric acids, sulphuric acid and other chemicals were purchased from Merck (India) Ltd. All chemicals were used without further purification.

2.3 Instruments and equipment

Electric oven, Magnetic stirrer (REMI 2 MLH), E-1 portable TDS & EC meter, pH-009(I)A pen type pH meter, sterilized 250ml separating funnels, sterilized conical flasks, sterilized 400ml beakers, watch glasses, 7'' funnels, glass rods, and 10ml measuring cylinders,

2.4 Extraction of waste fruit peels Orange (*Citrus sinensis*)

5 grams of Orange (*Citrus sinensis*) fruit peel powder with 50 mL of double-distilled water (DDW) taken in the 250 mL round bottomed flask, water condenser fitted and fix the running tap water then heated for 20 min at 80^o C. Then the extract was filtered with Whatman 1 μ filter paper. The filtrate was used to the further green synthesis of process.

2.5 Green synthesis of Silver nanoparticle (AgNPs) by waste fruit peels Orange (*Citrus sinensis*)

Silver nitrate (AgNO₃) solution of 0.1m M was prepared. Drop wise 10 ml of waste fruit peels extracts of Orange (*Citrus sinensis*) has been added and color changes were observed after 30 min[21]. and stirring at 500 rpm for 2 h at magnetic stirrer with heating instrument, to achieve precipitate containing final solution, The white colour reactant solution is turn to brownish black colour have shown in Figure:2. The obtained precipitate was filtered whatmann 1 μ filter paper. The nanopartricles containing filter paper was dried hot air oven and collect the air tight click lock tube. The green synthesised silver nanoparticles were characterised by UV,FTIR, FL, DLS, SEM, EDS and CV analysis.

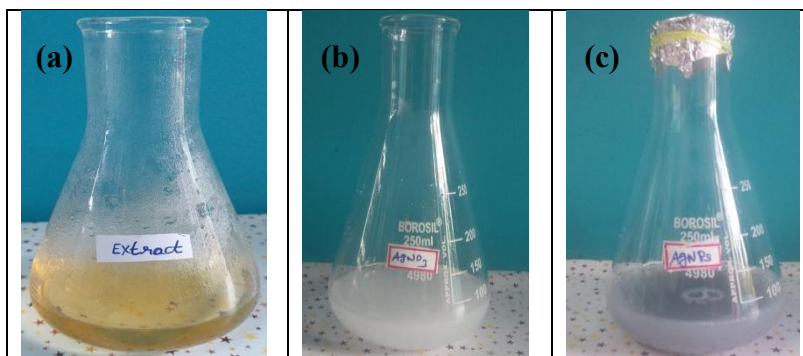


Figure:2, Green synthesis of silver oxide nanoparticles mediated by waste fruit peels Orange (*Citrus sinensis*)

III. CHARACTERIZATION

The absorption maximum of the silver oxide nanoparticles was measured by ultraviolet spectrum. The FTIR spectrum was recorded on Nicolet IS10 (Thermo Scientific, Waltham, MA) at room temperature. The IR spectrum was noted in the range of 400–4000 cm^{-1} . Different modes of vibrations were identified and assigned to determine the different functional groups present in the silver oxide nanoparticles by Orange (*Citrus sinensis*). Waste peel extract. Another one spectral studies carried out by fluorescence spectroscopy. DLS Analysis was used to measure the average size of the green synthesized nanoparticles, SEM analysis was done to visualise the shape as well as to measure the diameter of the green synthesized AgONPs. And additionally measured the reduction potential of the silver oxide nanoparticles by cyclic voltmeter studies.

IV. RESULT AND DISCUSSION

4.1 UV-Vis SPECTRAL ANALYSIS

It is well known that silver nanoparticles exhibit yellowish brown color in aqueous solution due to excitation of surface plasmon vibrations in silver nanoparticles. As the waste peel extract of orange fruit was mixed with aqueous solution of the silver nitrate, it started to change the color from watery to brown due to reduction of silver ion; which indicated the formation of silver nanoparticles. It is generally recognized that UV–Vis spectroscopy could be used to examine size and shape-controlled nanoparticles in aqueous suspensions. **Fig. 3** shows the UV–Vis spectra recorded from the reaction medium after heating the solution at 75 °C for 60 min. Absorption spectra of silver nanoparticles formed in the reaction media has absorbance peak at 438 nm and broadening of peak indicated that the particles are polydispersed.

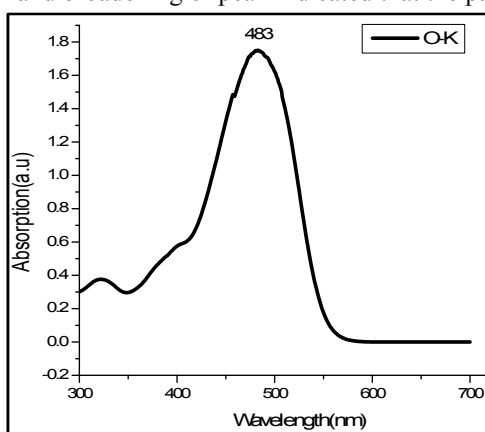


Figure 3: UV Spectrum of AgNPs by Orange peel extract

4.2 FT-IR spectral Analysis

The FTIR spectrum of AgNPs obtained in this study (Fig:4). FTIR measurement was carried out to identify the possible biomolecules responsible for capping and efficient stabilization of AgNPs synthesized using waste peel extract of orange fruit. In the FTIR spectrum of Orange peel extract capped AgNPs (Fig:4). FTIR measurements were carried out



to identify the possible biomolecules responsible for capping and efficient stabilization of the metal nanoparticles synthesized by waste peel broth. The peak IR bands observed at 3444.98 cm⁻¹ characteristic of the O–H stretching, 2923.46 and 2883.23 cm⁻¹ characterize alkane stretching vibrations, The band of 1644.84 cm⁻¹ have shown in and C=O stretching for carboxylic, aldehydic, ester, etc compounds and also indicates carbonyl stretch in proteins. The peaks at 1561.06 cm⁻¹ corresponds to amide rising due to. The strong peak at 1384.43-1194.41 cm⁻¹ corresponds to C–N stretching vibration of the amine with amide group. The peak of 1036.43 cm⁻¹, implying the binding of silver ions with hydroxyl and carboxylate groups of the extract, The peak near 848.19-780.36 cm⁻¹ is assigned to CH out of plane bending vibrations of substituted ethylene systems –CH,CH. In the case of nanoparticles, the peak of 606.74 cm⁻¹, reveals that Ag-O stretching vibrations .The spectra also illustrate a various functional groups in compounds of the orange peel extract have interacted with AgNPs surface making AgNPs highly stable.

4.3 Fluorescence spectroscopy

The fluorescence emission spectrum has been shown an obvious peak at 725.64 nm in AgNPs sample, shows no trend in neither the Stern-Volmer quenching plot nor the direct fluorescence method (Figure 5). Overall, even in the presence of AgNPs nanoparticles by orange waste peel aqueous extract.

4.4 DLS analysis

DLS is often interpreted to as a scattering of quasi-elastic light. It fulfills the role of size distribution and agglomeration of selective NPs. This process is quite sensitive, rapid and it can calculate the mean size of a particle on both macro and nano scale. The speed of the DLS technique is based on particle size. Small particles in suspension undergo random thermal motion known as Brownian motion. This random motion is modeled by the Stokes-Einstein equation. Below the equation is given in the form most often used for particle size analysis. The DLS analysis of green synthesized silver nanoparticle to shown the average size of the nanoparticle is 99.08 nm have shown in Figure:6. This result also shown in some of the nanoparticle having more than 100 nm, this is due to growth of the nanoparticle and aggregation of the two is more nanoparticles.

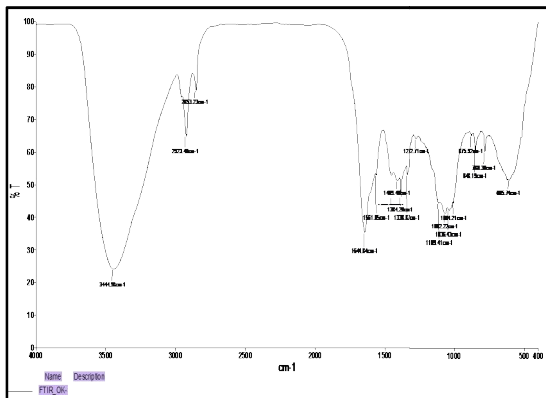


Fig:4 FTIR Spectrum of AgONPs

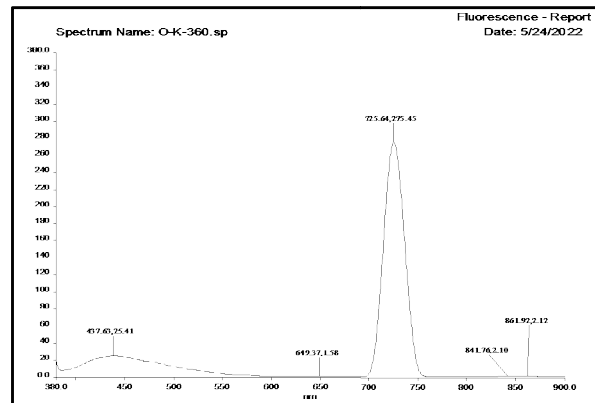


Fig:5 FL Spectrum of AgONPs

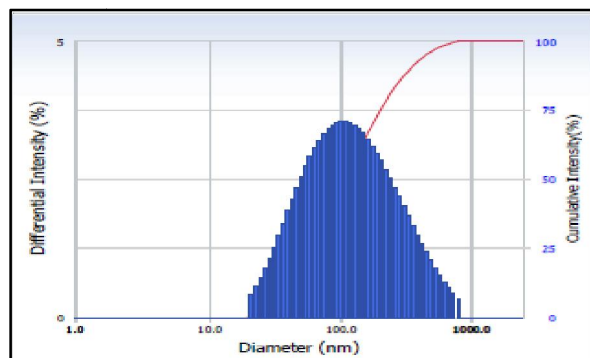


Figure 6: DLS-Spectrum of AgNPs by Orange peel extract

4.5 SEM analysis

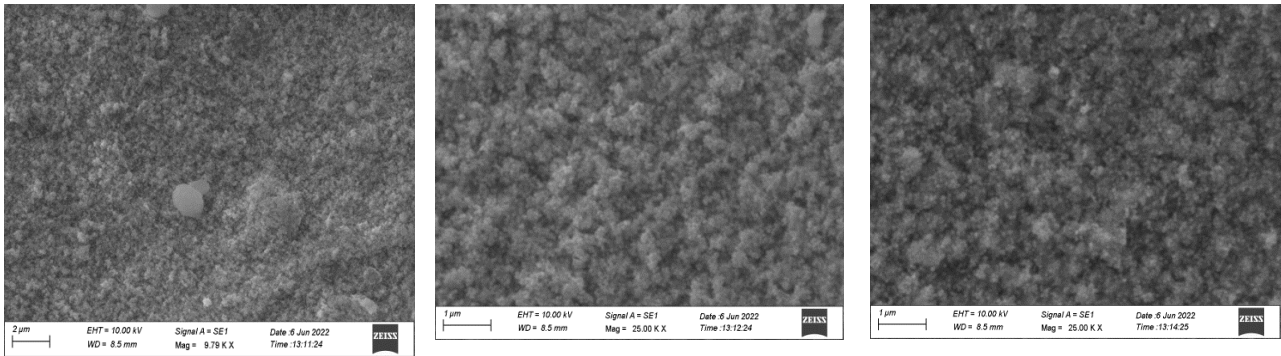


Figure 7: SEM Images of silver oxide nanoparticles by Orange peel extract

The morphology determined by SEM analysis of green synthesized Ag-nanoparticle by waste peel of orange fruit aqueous extract has shown Figure; 14a and 14 b. It can be seen from SEM image that AgONPs are agglomerated and not well formed. One can vividly see well defined nanoparticles with distinguish shapes. Specifically, SEM image for AgONPs reveal distinguishable rhomboid shaped nanoparticles, elongated nanorods and highly agglomerated nanoparticles.,AgONPs nanoparticles become well-formed revealing distinct shapes. To identify chemical elements and purity of synthesized samples Figure 6a shown in 2 μm Figure :6band 2 μm, Fig:6c has been shown 50 μm.

4.6. Cyclic voltammetry and discharge curve

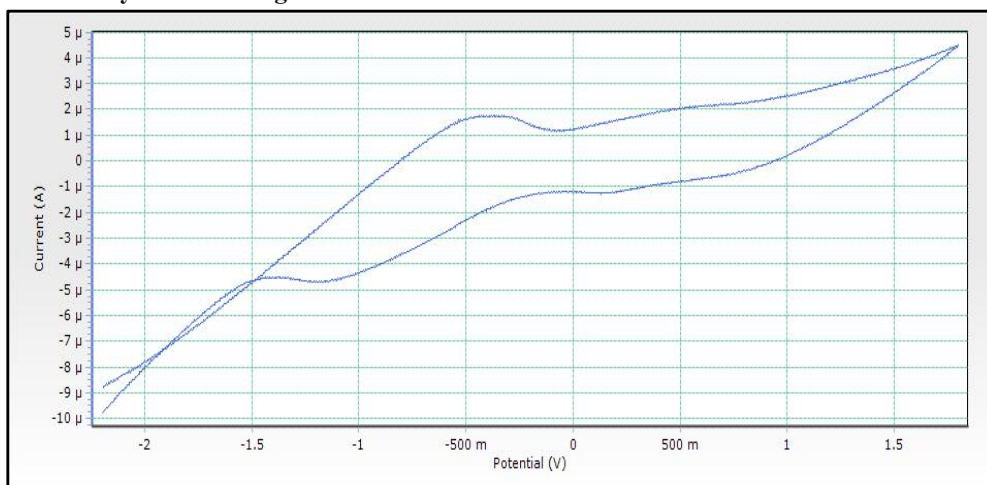


Figure 8: CV spectrum of cerium oxide nanoparticle by mango seed extract

The shape of the cyclic voltammetry curves is an ideal rectangular shape observed at 10 mV/s. Further increasing the scan rate the observed pattern of the CV curve is altered and it confirms the pseudo capacitive nature of the material The specific capacitance (SC) values of manganese ferriteelectrode can be estimated by using the formula $C_s = Q / m\Delta V$

Where, C_s is the specific capacitance, Q the anodic and cathodic charges on each scanning, m is the mass of the electrode material (mg) and ΔV is the scan rate (mVs^{-1}). Electrochemical measurements were performed in 0.2 tetra butyl ammonium perchlorate with a standard three electrode configuration consisting of a sample (working electrode), an Ag/ AgCl (reference electrode) and a high platinum wire (counter electrode). The scan rate increased in the range from 10 mV/s to 100mV/s and its corresponding specific capacitance values depicted in Fig.15 Further, the specific capacitance values of 290.4 F/g observed in the scan rate of 10 mV/s for the sample annealed at 700°C. The reason for high specific capacitance at low scan rate is observed in the present study suggested that the ionic diffusion takes place both inner and outer surfaces. The higher specific capacitance values observed in the present study confirm the good crystallinity of the silvernano particles.

V. CONCLUSION

The present study describe the green synthesis and characterization) of silver nanoparticles formed by orange peel extract. Each and every day, spoiling many billion tons of Peels in juice stalls, fruit juice company's, and direct eating in celebration and other places were consider peel is a waste one but this citrus fruit peel are contain various chemical constituents, and colouring materials This compounds are improved the drug delivery, discovery of colouring materials and perfumery products. The green synthesized silver nanoparticles are subjected to Ultra violet spectroscopy to identify the absorption maximum of metal nanoparticles. FTIR spectral analysis of silver nanoparticles have shown the metal oxide vibrations, and reduced peaks of all phytochemical constituents. Fluorescence spectra have shown in the florescence effect of the green synthesized silver nanoparticles. The DLS analysis and SEM analysis of green synthesized silver nanoparticles have shown the particles various magnifications and average size of the silver nanoparticles. Cyclic-voltammetry study have shown the electrical property of the silver nanoparticles by orange peel extract

REFERENCES

- [1]. Zarina., A. Nanda., *Int. J. Pharm. Technol. Res.*, **2014**, 6 (6), 1862–1869.
- [2]. Zarina, A. Nanda., *J. Pharm. Sci. Res.*, **2014**, 6(10), 321–327.
- [3]. D. Singh., V. Rathod., L. Fatima., A. Kausar., A. Vidyashree, N. B. Priyanka., *Int. J. Pharm. Pharm., Sci. Res.* **2014**, 4 (2), 31–36.
- [4]. D. Singh, V. Rathod, S. Ningangouda, J. Hiremath, A. S. Kumar, J. Mathew, *Bio.inorg. Chem. Appl.*, **2014**, 1–8.
- [5]. R. S. Bhosale, K. Y. Hajare, B. Mulay, S. Mujumdar, M. Kothawade., *Int. J. Curr. Microbiol. Appl. Sci.*, **2015**, 2, 144–151.
- [6]. S. Abdeen, S. Geo, S. Sukanya, P. K. Praseetha, R. P. Dhanya, *Int. J. Nano Dimension.*, **2014**, 5 (2), 155–162.
- [7]. M. Rai, A. Yadav, A. Gade, *Biotechnol. Adv.*, **2009**, 27, 76–83.
- [8]. P. Golinska, M. Wypij, A. P. Ingle, I. Gupta, H. Dahm, M. Rai., *Appl. Microbiol. Biotechnol.*, **2014**, 98 (19), 8083–8097
- [9]. A. Mohamedin, N. E. El-Naggar, S. S. Hamza, A. A. Sherief., *Curr. Nanosci.*, **2015**, 11, 640–654.
- [10]. S. Deepa, K. Kanimozhi, A. Panneerselvam., *Int. J. Curr. Microbiol. Appl. Sci.*, **2013**, 2(9), 223–230.
- [11]. S. Y. S. Lakshmi, H. Lakshmi, S. Sharmila., *World J. Pharm. Res.*, **2015**, 4 (7), 1592–1611.
- [12]. N. E. El-Naggar, N. A. M. Abdelwahed, *J. Microbiol.*, **2014**, 52 (1), 53–63.
- [13]. S. Iravani., *Int. Scholarly Res. Not.* **2014**, 1–18.
- [14]. H. Yue, J. Chen, E. Sandvol, J. Ni, T. Hearn, S. Zhou, Y. Feng., Z. Ge, A. Trujillo, Y. Wang, G. Jin, M. Jiang, Y. Tang, X. Liang, S. Wei, H. Wang, W. Fan., *J. Geophys. Res.*, **2012**, 117, 1–18.
- [15]. G. S. Kiran, T. A. Thomas, J. Selvin, B. Sabarathnam, A. P. Lipton, *Bioresour. Technol.*, **2010**, 101, 2389–2396.
- [16]. G. Christina, V. Dirk, I. Arnout, **2003**, 19 (17), 6693–6700.
- [17]. P. Jorg., **2015**, 17 (36), 6809–6830.
- [18]. P. S. R. Krishna, K. Sanjeev., *Nano. Tec.*, **2013**, 29 (31), 9863–73.
- [19]. H. Chenhui, W. Dingsheng, Z. Wen, P. Qing., *J. Mat. Res.*, **2011**, 24(2), 352–356.
- [20]. X. Dong, X. Ji, J. Jing, M. Li, J. Li, W. Yang., *J. Phys. Chem. C.* **2010**, 114 (5), 2070–2074.
- [21]. Dwivedi, A.D., Gopal, K., 2010. Biosynthesis of silver and gold nanoparticles using *Chenopodium album* leaf extract. *Colloids Surf.*, A 369, 27–33.