

Green synthesis of phosphorous nanoparticles using seed extract of *Caesalpinia Bonducella* and their new avenues in nano science

Sathammai Priya N*, Ambikapathy V, Panneerselvam A, Senthilkumar G

PG, Department of Microbiology, A.V.V.M Sri Pushpam College (Autonomous), Poondi, Thanjavur, Affiliated to Bharathidasan University, Tamil Nadu, India

Abstract

Objective: Of-late, there is an abundant usage of synthesized metal nanoparticles of silver, gold, platinum, etc. in the field of medicines and physics. As these nanoparticles are metal and when they are used as medicine for therapeutic purposes, they become toxic. Hence, a maiden attempt has been made for nanoparticle synthesization using phosphorous for avoiding metal. Here, the present study is about using the seed extract of *Caesalpinia bonducella* synthesized phosphorous nanoparticle (PNPs) for the first time, that an eco-friendly manner.

Methods: The PNPs were synthesized using *Caesalpinia bonducella* seed extracts and the synthesized PNPs were characterized by ultraviolet (UV)–visible spectrophotometry, Fourier-transform infrared (FTIR) spectroscopy, X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis.

Results: Synthesis of nanoparticles was confirmed and ascertained by visual detection in which the orange coloured solution gets changed to a brown colour. Further, a combination of spectroscopic and microscopic techniques were used to characterize the synthesized nanoparticles via UV- Vis Spectroscopy, FTIR, XRD and SEM analysis. Significant absorption was observed at 279 nm resulting in the formation of nanoparticles. FTIR analysis was performed to identify the biomolecules, which played a key role in the reduction of phosphorous. The XRD and SEM result revealed a crystalline nature of PNPs.

Conclusion: This approach has proven that PNPs can be synthesized by using seed extract in which biomolecules effectively act as capping and reducing agent.

Keywords: phosphorous nanoparticles, green synthesis, *Caesalpinia Bonducella*, FTIR, XRD, SEM

Introduction

Nano materials as those which have structured components with at least one dimension less than 100nm. Nanotechnology is a broad-based science involving manipulation of atoms, electrons, protons and neutrons in a variety of ways to generate understanding of how materials can be developed to solve many problems in medicine, engineering, agriculture, biology, chemistry, surface science, space exploration, ocean and marine science, geography and geology. In some cases the research will develop new machines or ways to deliver new products (Kawazoe *et al.* 2005) [8]. The nanoparticles are of different shape, size, and structure. It be spherical, cylindrical, tubular, conical, hollow core, spiral, flat, etc., or irregular and differ from 1nm to 100nm in size. In the new millennium, we have novel biological targets which are defined at the molecular level, which have incredible success in comprehending human illness. (Acquiline Rosy *et al.* 2020) [7]. The surface can be a uniform or irregular with surface variations. Some nanoparticles are crystalline or amorphous with single or multi crystal solids either loose or agglomerated (Macado S *et al.* 2015).

Nanoparticles can be used in drug delivery and in the determination of drugs in pharmaceuticals (Saleh *et al.* 2014) [15]. The total drug consumption and side effects are significantly lowered by placing the drug in the required area in required dosage. This method reduces the cost and side effects (Mudshinge *et al.* 2011) [12]. Phosphorous is one of the essential elements required for growth of plants, animals and microorganisms (Tiessen *et al.* 2008) [5]. The

organic phosphorous compound deoxyribonucleic acid provides the genetic code for life and adenosine triphosphate (ATP) is essential for cellular energy conversion. (Tarafdar *et al.* 2012) [21]. the continuous production of phosphorous is based only on non-renewable resources, results in significantly increased cost and availability for future. So there is an urgent need to develop technology for efficient phosphorous utilization and its sustainability.

Green synthesis of metal nanoparticles has been reported in many research papers. The non-metal nanoparticles synthesization is a topic of debate and is not well understood. Metals which are the most commonly used for synthesis of nanoparticles using plant seed extract (Rakes vargeese *et al.* 2019) stem bark extract (Srinivasa Rao *et al.* 2016) [20] Leaf extract (Kumara swamy *et al.*, 2015) [9]. Plant crude extracts contains novel secondary metabolites such as alkaloids, flavonoids, saponins, steroids and tannins in which these compounds are mainly responsible for the reduction of ionic into bulk nanoparticles formation (Aromal *et al.* 2012) [2]. Recently many studies have proved that the plant extracts act as a potential precursor for the synthesis of nanomaterial in non-hazardous ways. Since the plant extract contains various secondary metabolites, it acts as reducing and stabilizing agents for the bio reduction reaction to synthesized novel Nano particles (Palaniselvam kuppusmy *et al.* 2016). The rich biodiversity and easy availability of plant entities have been highly explored for the nanomaterial synthesis (Monda *et al.* 2011) [11]. Hence, eco-friendly synthesis of nanoparticles is considered as

building blocks of the forthcoming generations to control various diseases (Cruz *et al.* 2010) [4].

In this present work, a seed extract of *Caesalpinia bonducella* was used as reductant and stabilizer for phosphorous nanoparticles. The seed contain various chemical constituents such as Silicic Acid (H₄SiO₄), Tetraethyl Ester, 1,2-Benzenedicarboxylic Acid, Diethyl Ester, Benzene, 1,2,4-Trimethoxy-5-(1-Propenyl)-, (Z)-, 1-Undecanol, 1- Tetradecanol, Acrylate, Tetradecanoic Acid, Benzene, Ethylphenoxy-, Phenol, 2-(1-Phenylethyl)-, Pentadecanoic Acid, 2,4-Decadienamide, N-Isobutyl-, (E,E)-, N-Hexadecanoic Acid, Benzenecarbothioic Acid, 2,4,6-Triethyl-, S-(2- Phenylethyl) Ester, Hexadecanoic Acid, Ethyl Ester, Heptadecanoic Acid, N-Nonadecanol-1, 9,12-Octadecadienoic Acid (Z,Z)-,9-Octadecenoic Acid, (E)-, Phenol, 2,4-Bis(1-Phenylethyl)-, 2-Hydroxy-4-Methoxy-7-Methyl-7,8,9,10,11,12,13,14- Octahydro-6-Oxabenzocyclododecen-5-One, Phenol, 2,4-Bis(1-Phenylethyl)-, Pregn-4-En-17(Alpha),20(Alpha)-Diol-3-One, Piperine, Fucosterol (Sathammai Priya *et al* 2019) [18].

Not even a single day passes without any new findings in the realm of medicine and science. Innovative ideas and new concepts are pouring in from everywhere, resulting in an in depth research. The outcomes are at times amazing, astounding and also outstanding. Nano Science is not an exception to this. From small steps to big measures, Nano has taken a giant leap, with its exponential growth and dynamic changes. The seed of *Caesalpinia bonducella*, commonly known as Kalicikkai in Tamil is immensely used for the therapeutic purpose. The seed indeed is the need of the hour. It is the seed for the new revolutions in the field of research. Till date, there has not been systematic study carried out, on the seed of *Caesalpinia bonducella*. Hence, in the present investigation, we have tried to explore a rapid cost effective, ecofriendly and readily reproducible approach for the purpose of scale –up and subsequent easy downstream processing for the production of efficient phosphorous nanoparticle using Hypo phosphorous acid (H₃PO₂) employing *Caesalpinia bonducella*. Besides, an effort to understand the entire gamut of Nano-transformation mechanism has been made.

Material and Methods

Plant material and preparation of extract

The *Caesalpinia bonducella* seed sample was collected from Viramathi, a small village in Tamil Nadu, India. The plant seed was authenticated at Rapinat Herbarium of St. Josephs College, Tiruchirappalli. The seed was subjected to air drying at room temperature to prevent the denaturing of some active principles. After drying, it was ground to increase the surface area. The powdered sample was thereafter soaked in Ethanol at seed material to solvent ratio 1:10 w/v for 72 hours at room temperature with frequent manual agitation.

Synthesis of Phosphorous nanoparticles

About 10g of dry plant seed powder was added to 100ml of double distilled water and boiled at 50-60°C for 10 min. The obtained extraction was filtered using Whatmann No.1 filter paper. Moreover, 0.1M of Hypo phosphorous and source materials were dissolved in 100ml of seed extract. The mixture solution could be stirred constantly at 80°C for 6h. Brown precipitates were formed on continuous stirring and Nano powder was heated at 120°C. The precipitated

Nanoparticles were lyophilized. Lyophilized Nano particles were stored in a cool, dry and dark place and further their characterization was carried out.

Characterization of synthesis Nano particles

UV was used to obtain UV-Visible spectra of PHNPs at different time intervals using seed extract diluted with water (1:10) as a blank. Further the shape and size of the formed Nanoparticles were determined by FTIR, XRD and SEM. Presence of functional groups present in PHNPS was determined by using FTIR. Four per centimeter resolution was taken in all spectra with 400- 4000 cm⁻¹ IR range. The crystalline nature of PHNPS was confirmed by XRD pattern obtained from (Rigaku D/ Ma- 2500, Japan). The sample was prepared by crushing the freeze dried PHNPS. The samples were analyzed at 25° C temperature using a Cu k α -1. X-ray source with a wavelength (λ) of 1.5443Å°. The angle of incidence was varied from 10° to 80° at a step of 0.05° and scanning rate of 10°/ min. A lyophilized sample of PHNPs was subjected to Scanning Electron Microscope at 10kV to study the morphological features of phosphorous nanoparticles.

Results and Discussion

UV- Visible Spectroscopy

Nano Particles synthesis initiates once the *Caesalpinia bonducella* seed extract was introduced into 0.1M of Hypo phosphorous.

The gradual colour change of phosphorous/ seed solution from orange to brown indicates the formation of Phosphorous nanoparticles as shown in (Fig. 1). Formation of nanoparticles in the aqueous solution was further confirmed by the UV- Visible spectroscopy. The wavelength scale was fixed between 200 and 1100 nm, and the solution was scanned in this range. Maximum absorbance at 262.5nm was observed, which is the characteristic of phosphorous nanoparticles (Ashutosh Tiwari *et al*, 2012) [1]. The curve (Fig. 2) shows an increase in absorbance with the increase in incubation time (30 min, 45 min and 1hr) of hypo phosphorous and seed extract.



Fig 1: Visual Detection of the solution before bio-reduction (left) and after bio-reduction (right)

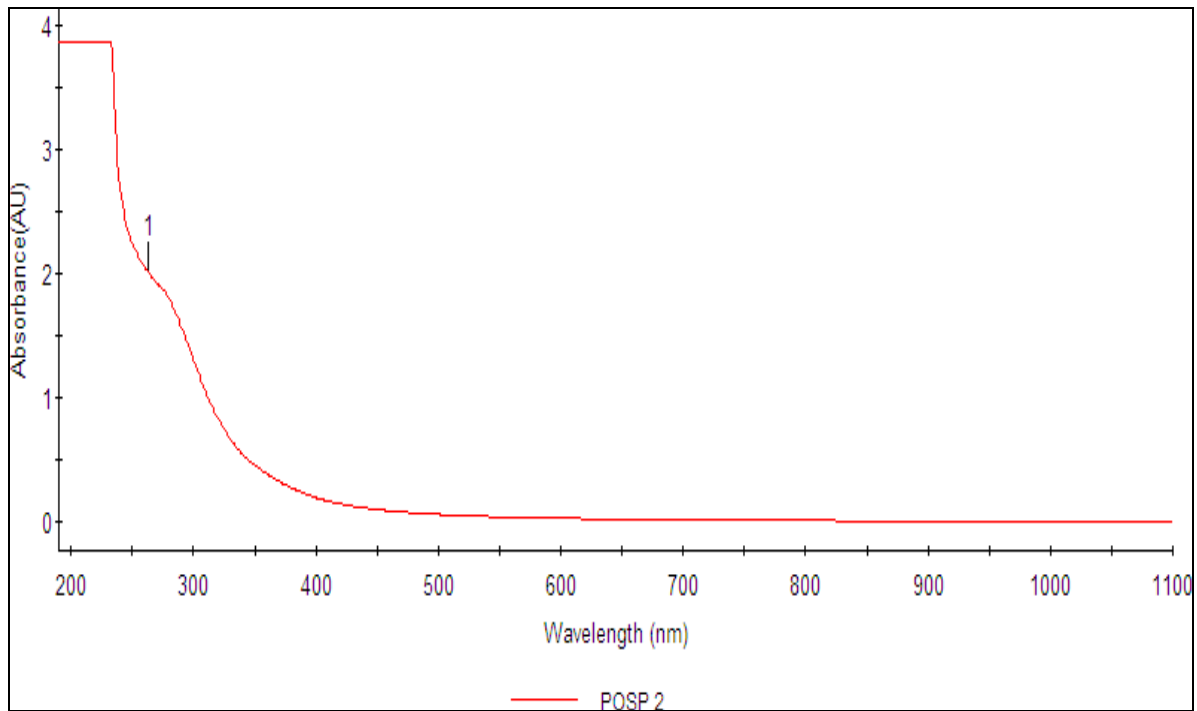


Fig 2: Absorption spectra of Phosphorous nanoparticles using seed extracts of the *C.bonducella*

FTIR Analysis

FTIR has become an important tool in organic chemistry because it is enabling to identify different functional groups. The FTIR spectrum of plant seed is represented in (Fig. 3). The peak values obtained from FTIR analysis revealed probable functional groups present on the seed powder. A broad peak observed at 3353.15cm⁻¹ could be assigned to

the O- H stretching vibrations (Sangu *et al* 2018) [17]. The medium peak at 1548.38 represents the deformation and stretching band of functional groups with NH bonding (Bharathi *et al* 2017). The distinct absorption peaks observed at 1651, 1548 and 1241 cm⁻¹ are assigned as amide C=O, N-H and C-N bands, respectively (Salem *et al* 2016) [16].

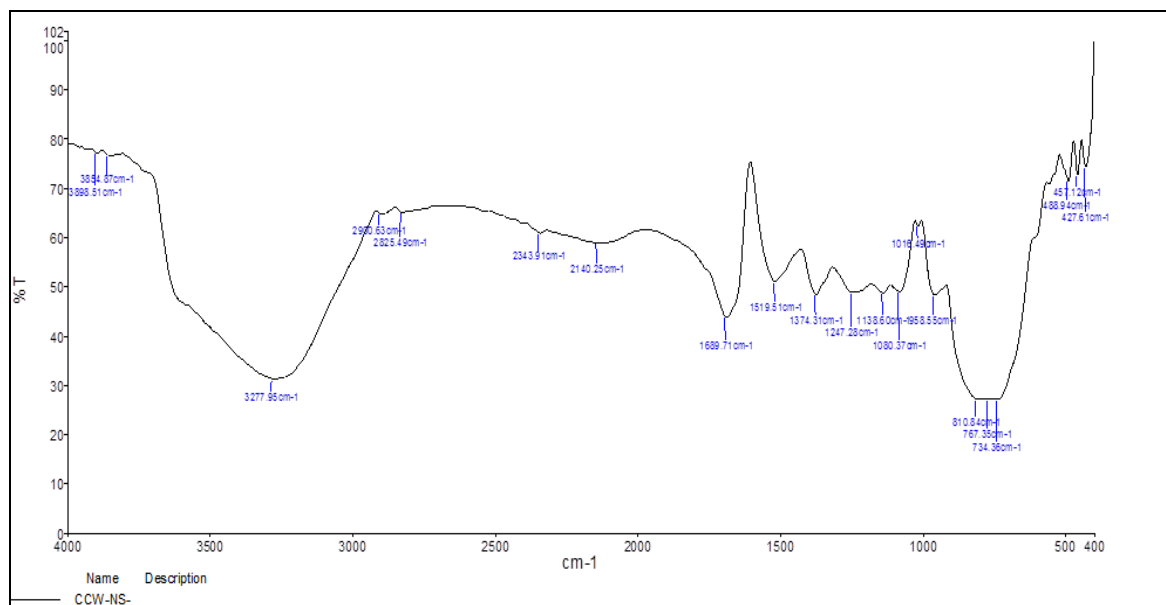


Fig 3: FTIR spectra of Phosphorous nanoparticles using *C.bonducella* seed extract

These characteristics absorption peaks are shifted to higher and lower frequency side in the green synthesized Nano phosphate displayed in (Fig. 3). P-O stretching modes of phosphate groups at 1.077 and 1.048 cm⁻¹ were observed for the seed powder. The symmetric P-O stretching mode for phosphate group occurs at 958cm⁻¹ and this was confirmed by (Hongquan *et al* 2002). The peaks at 1023 and 578cm⁻¹ for PO₄-3 groups appear in seed powder. Where as

in Nano phosphate compound P-O symmetric stretching (1138cm⁻¹), asymmetric stretching (1247 cm⁻¹), symmetric bending (488 cm⁻¹) and asymmetric bending (734 cm⁻¹) modes are appeared in (2,4). This may be due to the fact that in Nano size grains the atomic arrangements on the boundaries differ greatly from that of bulk crystals resulting in the shifting of IR active modes. In the present case, all the

IR active modes are shifted to the high frequency side, mainly because of the Nano grain size of the sample.

XRD Analysis

The XRD patterns of PHNPs indicating the crystalline nature of biosynthesized phosphorous Nanoparticles as confirmed by the corresponding peaks (4) with respect to Bragg's model of diffraction given by the Joint Committee on powder diffraction standards (JCPDS). The sample crystalline (XCR) was determined (Table 1) by using the height of the 153 peak (I 153, $2\theta = 28.27^\circ$) and the lower height between the 200 and 112 peaks (IAM, $2\theta = 40.4^\circ$). I

200 represent both crystalline and amorphous material while IAM represents only the amorphous material (Segal *et al* 1959) [19]. The collected XRD data was perfectly matched with standard ASTM data (JCPDS -09-0432) and calculated crystallite size was very small from 25-60nm.

Table 1: The XRD pattern of PHNPS

Pos. [2θ .]	Height [counts]	FWHM Left [2θ .]	d-spacing [Å]	Rel. Int. [%]
28.2794	153.90	0.1968	3.15587	100.00
40.4689	83.83	0.1968	2.22903	54.47
66.8540	4.16	1.5744	1.39948	2.71

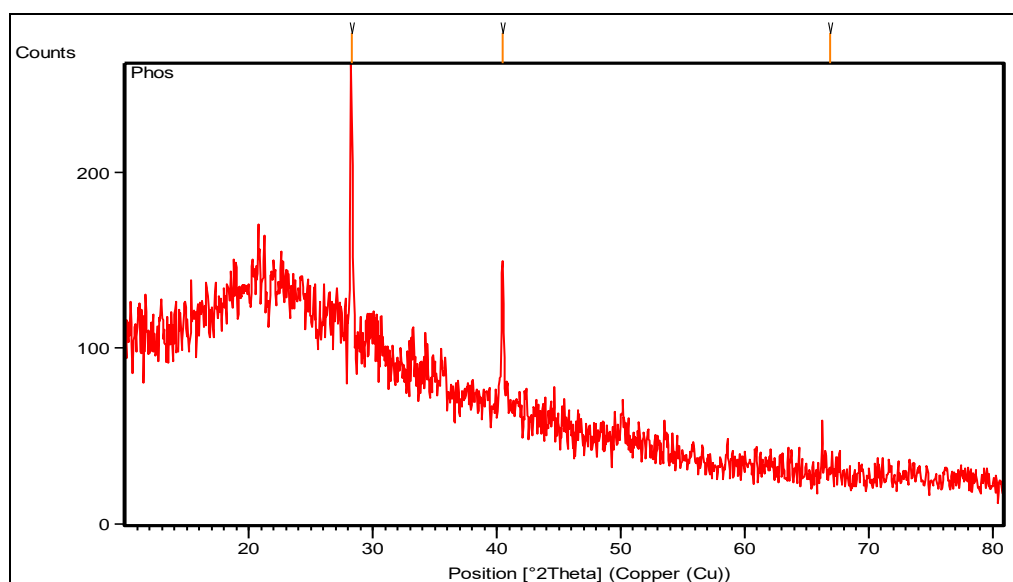


Fig 4: XRD image of Phosphorous nanoparticles using *C. bonducella* seed extract SEM Analysis

The synthesized nanoparticles were characterized using SEM. (Fig.5) illustrates the SEM image of the Nanoparticles at a magnification of 3.06 XV. The particles were found to

be very crystalline form in nature. 3D Structures of the synthesized Nanoparticles were confirmed by the SEM image

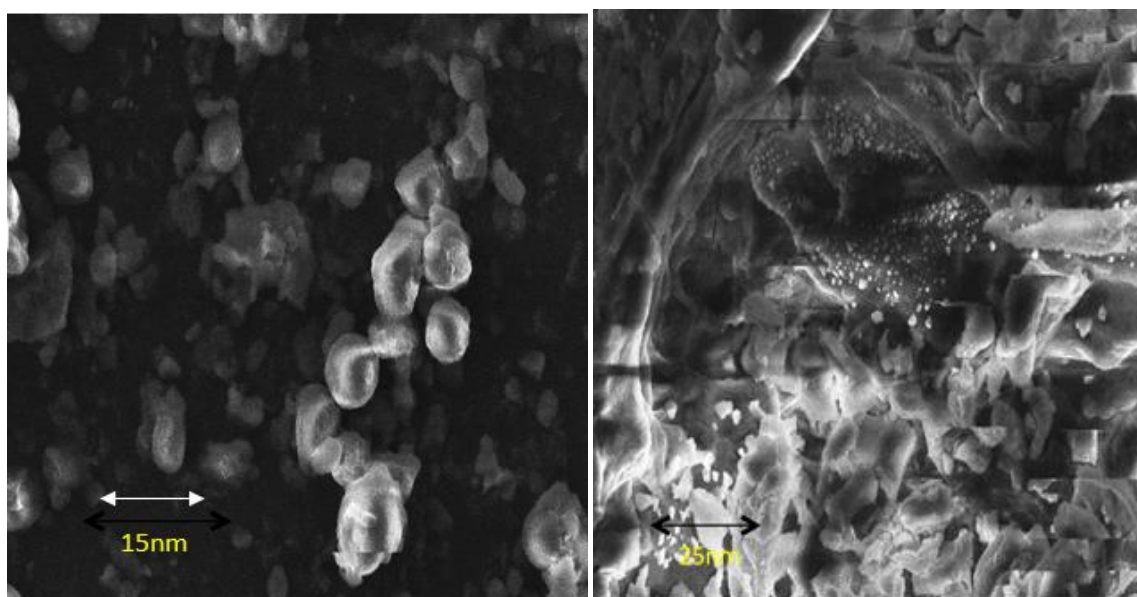


Fig 5: SEM Analysis of Phosphorous Nano particles of *C. bonducella* seed

Conclusion

Phosphorous nanoparticles were successfully synthesized using the extract of medicinal *Caesalpinia bonducella* seed. This low cost and environmentally benign extract of

Caesalpinia bonducella served as a potential stabilizing and reducing agent. The formation of PHNPs was first confirmed by orange colour due to the peak in the UV-Visible spectrum observed at 260 nm. The resulting PHNPS

was characterized by FTIR, XRD, and SEM. FTIR spectrometry confirmed the presence of functional biomolecules. The crystalline nature of PHNPS was determined by XRD and SEM. Finally, this diligent study has brought to light an assuring fact, the fact about the synthesized PHNPs. And they are therefore recommended as product of value in the field of nanotechnology and Nano medicine.

Conflict of Interest

The author's declared that they have no conflict of interest

Reference

1. Ashutosh Tiwari, Ajay K, Mishra, Histoshi Kobayashi, Anthony PF, Turner. Intelligent Nanomaterial's: process, properties and Applications, 1st edn. Wiley, 2012, 39-148.
2. Aswathy Aromal, Daizy Phillip. Green synthesis of gold nanoparticles using *Trigonella foenum – graecum* and its size dependent catalytic activity. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2012, 1-5.
3. Bharathi V, Janathul Firdous, Noorzaid muhamad, Resi Mora. Green synthesis of *Magnifera indica* silver nanoparticles and its applications using Fourier Transform Infrared and scanning electron Microscopy. National journal of pharmacy and pharmacology. 2017; 7(12):1-5.
4. Cruz D, Fale PL, Mourato A, Vaz PD, Serralheiro ML, Lino ARL *et al.* Preparation and physiochemical characterization of Ag nanoparticles biosynthesized by *Lippia Citriodora* (lemon Verbena) Colloid Surf B, 2010, 67-73.
5. Holm Tiessen. Phosphorous in the global environment. Plant Eco physiology Springer, Dordrecht, 2008, 7.
6. Hon Guan, Yin-jung chen, Yew-chaye loo, Yi-Minie, Grant P Steven. Bridge topology optimization with stress, displacement and frequency constraints. Computers & Structures. 2002; 81(3):131-145.
7. Acquiline Rosy P*, Jebastin Sonia Jas M, Santhanalakshmi K, Muthukumar S. Green synthesis, biological evaluation, and density functional theory calculations of thiazolidinone derivatives – A review. Asian J Pharm Clin Res. 2020; 13(1):10-20
8. Kawazoe T, Kobayashi K, Takubo S, Ohtsu M. Nonadiabatic photo dissociation process using an optical near field. J Chem physics. 2005; 122(2):024-715.
9. Kumara Swamy M, Sudipta KM, Jayanta K, Balasubramanya S. The green synthesis characterisation and evaluation of biological activities of Silver nanoparticles synthesized from *Leptaclenia reticulate* leaf extract. Applied nanoscience. 2015; 5(1):73-81.
10. Machado S Pacheco JG, Nouws HP, Albergaria JT, Delerue-Matos C. Characterization of green Zero-Valent iron Nanoparticles produced with tree leaf extracts. Sci. Total Environ. 2013; 445-446:1-8.
11. Monda S, Roy N, Laskar RA, SK I, Basw S, Mandal D *et al.* Biogenic synthesis of Ag,Au and biometallic Au/Ag alloy nanoparticles using aqueous extract of mahogany leaves. Colloid Surf B. 2011; 82:497-504.
12. Mudshinge SR, Deore AB, Patil S, Bhalgat CM. Nanoparticles: Emerging carriers for drug delivery. Saudi Pharm J. 2011; 19(3):129-41.
13. Palaniselvam Kuppusamy, Mashitah M, Yusoff, Gwanty Pragas Maniam, Natanamurugaraj Govindam. Biosynthesis of metallic nanoparticles using plant derivatives and there new avenues in pharmacological application- An updated report. Saudi Pharamaceutical Journal. 2006; 24(4):473-484.
14. Rakes Varghese, Mohammed A Almalki, Soundararajan Ilavenil, Jayamthi Rebecca, Choon Choi. Silver nanopaticles synthesized using the seed extract of *Trigonella foenum-graecum* L. and their antimicrobial mechanism and anticancer properties. Saudi Journal of Biological Sciences. 2019; 26(1):148-154.
15. Saleh TA. Detection: From Electrochemistry to Spectroscopy with Chromatographic Techniques, Recent Trends with Nanotechnology, Detection. 2014; 2: 27-32.
16. Salem MN, Albanna LS, Awwad AM, Ibrahim QM, Abdeen AO. Green synthesis of Nano- Size Sulfur and its effect on plant growth. Journal of agricultural Science. 2016; 8(1):188-194.
17. Sangu V, Priyadharshini. Evaluation of Adsorption capacity of prosopis juliflora seed powder for removal of trace elements from aqueous solution. Asian Journal of Chemistr. 2018; 30(11):2462-2466.
18. Sathammai Priya N, Ambikapathy V, Panner Selvam A, Sangeetha K. Gas chromatography and mass spectroscopy analysis of phytoactive components on the seed extract of *Caesalpinia bonducella*. Research J and Pharm and Tech. 2019; 12(10):4628-4634.
19. Segal LGJMA, Creely JJ, Martin Jr AE, Conrad CM. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. Textile Research Journal. 1959; 29(10):786-794.
20. Srinivasa Rao N, Rao MVB. Green Synthesis Charac, and biological studies on Silver nano particles from C.b stem bark extract. Der Pharma Chemica. 2016; 8(18):14-19.
21. Tarafdar, Ramesh Raliya, Indira Rathore Microbial Synthesis of Phosphorous nanoparticle from tri-Calcium Phosphate using *Aspergillus tubingensis* TFR-5. Journal of Bionanaoscience. 2012; 6(2):84-89.