EXTRACELLULAR FACILE SYNTHESIS OF SELENIUM NANOPARTICLES INVOLVING *MANILKARA ZAPOTA*

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Abstract

Biogenic nanomaterials play an important role in design a novel biological technique for the synthesis of selenium nanoparticles using aqueous leaf extract of *Manilkara zapota*. The newly synthesized selenium nanoparticles, UV, XRD, TEM analysis, FTIR etc. UV spectrum exhibited an absorption peak at 286 nm. X-ray diffraction pattern displayed typical peak of crystalline at 100, 101, 110, 102 and 201. The transmission Electron Microscopy result indicates that the most of formed selenium nanoparticles are in nature geometric spherical, oval structure.

Keywords*:* Facile Synthesis, Selenium nanoparticles, *Manilkara zapota,*

1. Introduction

Nanotechnology can be defined as the science and engineering involved in the design, synthesis, characterization and application of materials and devices whose smallest functional organization in at least one dimension is on the nanometer scale (one-billionth of a meter) (Emerich and Thonos 2003; Sahoo and Labhasetwar 2003). In the past few years' nanotechnology has grown by leaps and bounds, and this multidisciplinary scientific field is undergoing explosive development (Williams, 2004; Cheng, *et al*., 2006; Chan, 2006). It can prove to be a boon for human health care, because nanoscience and nanotechnologies have a huge potential to bring benefits in areas as diverse as drug development, water decontamination, information and communication technologies, and the production of stronger, lighter materials. Human health-care nanotechnology research can definitely result in immense health benefits.

Synthesis of nanoparticle is usually conceded out by various physical and chemical methods such as laser ablation, pyrolysis, chemical or physical vapour deposition, sol-gel and lithography electro deposition and most of them are expensive and require the use of toxic solvents. Nowadays, there is a growing need to develop eco-friendly processes, which do not use toxic chemicals in the synthesis protocols.

Green synthesis approaches include mixed-valence polyoxometalates (Zhou, *et al.*, 2010), polysaccharides (Huang and Yang, 2004), biological, and irradiation method which have advantages over conventional methods involving chemical agents associated with environmental toxicity. On the contrary, selection of solvent medium and selection of eco-friendly nontoxic reducing and stabilizing agents are the most important issues which must be addressed in green synthesis of nanoparticles and therefore attention of the researcher is shifted from physical and chemical processes towards green chemistry and bioprocesses (Mohanpuri, *et al.*, 2008; Iravani, *et al.*, 2014)

Furthermore, the integration of principles of green chemistry to nanotechnology has become a key area in nanoscience and has received great attentions in recent years. In this piecing together, efforts are made to use eco-friendly methods for the synthesis of noble metal nanoparticles (Hubental, *et al.*, 2008) and it is achieved mostly by the use of plants (Makarov, *et al.*, 2014) wherein, these green methods are low cost, fast, efficient and generally lead to the formation of crystalline nanoparticles with varied sizes. This depends on the nature and concentration plant extract. Moreover, it also depends on their pH, temperature and incubation time synthesis reaction (Noruzi, 2015).

Based on the foregoing facts in this present investigation an attempt was made to synthesize selenium nanoparticles using green chemistry approach.

Selenium is one of the essential trace elements in the body in due to its anti-oxidative as well as pro-oxidative effect and has great importance in nourishment and medicine (Zhang, *et al.*, 2004). Se has one of the narrowest ranges between dietary deficiency (40 lg day-1) and toxic levels (400 lg day-1). The Se field is expanding at a rapid pace and has grown dramatically in the last years. Selenium is a key player in cellular metabolism, an essential component of enzymes that protect the body against free radical species and has important roles in metabolism of thyroid, human fertility and many other vital functions. All aspects of Se in biology have advanced in various fields such as genetic, biochemical, molecular, and health areas.

In particular, selenium nanoparticles (SeNPs) have excellent bioavailability, high biological activity and low toxicity. For instance, consumption of 200µg Se per day by cancer patients reduces mortality and depresses the incidence of many diseases including lung, colorectal and prostate cancers (Wang, et al., 2007; Zhang, *et al.*, 2001; Pagmantidis, *et al.*, 2008).

A reproducible but simple method of preparation of stable selenium nanoparticles with biomedical application is still a challenge. Both reduction and oxidation techniques can be employed to prepare selenium nanoparticles. The main synthetic approach for preparing selenium nanoparticles

ISSN: 2278-4632
Vol-14, Issue-9, September: 2024

is by chemical reduction, employing reducing agent and stabilizer. However, the use of stabilizer may hinder the normal utilization of synthesized nanoparticles in biological applications and further stabilizer may have toxic potential due to its chemical nature. The present study reports a simple phytochemical mediated green synthesis of selenium nanoparticles and their physico chemical features. Accordingly, the following are the objectives addressed in the present investigation:

- Biological synthesis of selenium nanoparticles using green chemistry approach.
- Demonstration of physicochemical nature of newly formed selenium nanoparticles.

2. Materials Methods

Medicinally important plant materials such as leaves, flowers etc., were subjected in the present investigation in order to generate pharmacologically important selenium nanoparticles. Among the subjected plants different parts leaf extract of *Manilkara zapota* found to possess the synthesis property of selenium nanoparticles.

2.1. Preparation of *Manilkara zapota* leaf extract

To prepare *Manilkara zapota* leaf extract; 5g of *Manilkara zapota* leaves were washed thoroughly with tap water and followed by deionised water. The leaves were ground with mortar and pestle, by using 50 ml of deionised water the plant extract was prepared. The extract was filtered using whatman No.1 filter paper. Freshly prepared *Manilkara zapota* leaves extract was used for the synthesis of selenium nanoparticles. Freshly prepared extract alone has been used throughout the study.

2.2. Synthesis of selenium nanoparticles

In this experiment, 20 ml of fresh leaves extract was taken in a 250 ml beaker. Different concentrations were examined to identify the particular concentration which reduces the sodium selenite to selenium ions. The aqueous extract obtained in this manner used as a precursor for synthesis of selenium nanoparticles. Among the various concentrations, 0.173g (10 mM) of sodium selenite was dissolved in 100 ml of deionised water. This is considered as stock solution. The plant extract (20 ml) is kept under “magnetic stirrer” for 40 minutes, then into this 100 ml of prepared stock solution

(Sodium selenite) was added dropwise. The sodium selenite was reduced to selenium nanoparticles by using *Manilkara zapota* leaf extract. The formation of selenium nanoparticles (SeNPs) has been observed by the appearance of reddish orange colour.

2.3. Characterization

Selenium nanoparticles synthesized by of sodium selenite (Na_2SeO_3), with the *Manilkara zapota* plant's leaf extract was characterized using X-Ray Diffraction (XRD), UV-vis spectroscopy (UV), Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy and Scanning Electron Microscopy with Energy Dispersive X-Day method (SEM&EDX).

3. Results

Nanomaterials functionality being determined by their physicochemical properties, accordingly scientists actively involved in developing newer synthesis protocol for nanomaterials with varying characters such as size, shape, surface chemistry etc., Among the emerging relevance of nanomaterials in various fields, predominantly, application on life science is mentionable. Therefore, it has been emphasized that development of biocompatible nanomaterials is imperative (Sharma *et al*., 2009; Narayanan and Sakthivel, 2010).

Large numbers of medicinal plants with pharmacological background were screened out and collected from Thiruvalluvar University campus herbal garden, Vellore, Tamil nadu, India pinpoint their bioreduction property of selenium ions into selenium nanoparticles. The main reason for choosing medicinally important plants for synthesis is to generate selenium nanoparticles with medicinal implication. Amongst the various reaction mixture of different plant's parts leaf extract of *Manilkara zapota* identified as a potential candidate for synthesizing selenium nanoparticles. *Manilkara* is genus of trees in the family *Sapotaceec*.

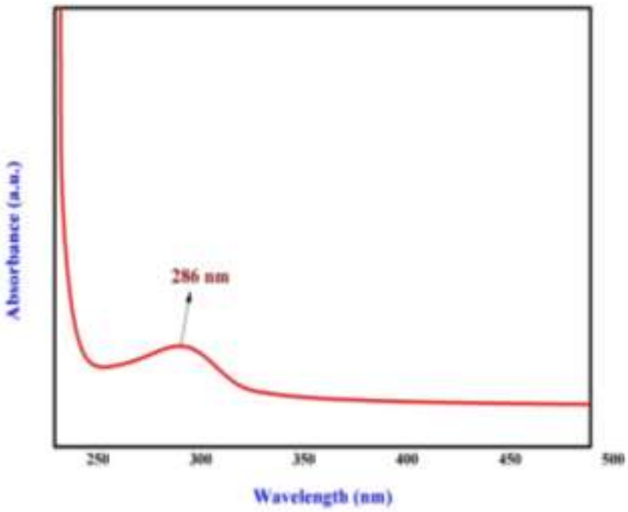
Five grams of leaf of *Manilkara zapota* which was macerated with 50 ml of de-ionised water, then it was filtered. The filtrate was used for synthesis. The precursor sodium selenite was prepared at the concentration of 10mM. 20ml of aqueous plant extract was kept in stirring condition. After 10 mins of stirring condition the 100ml of precursor sodium selenite was added to the leaf extract dropwise. After 40 mins of such experimental condition the change of colour from yellow to reddish orange was appeared, which indicates the formation of selenium nanoparticles (Figure 1).

ISSN: 2278-4632
Vol-14, Issue-9, September: 2024

The formation of selenium nanoparticles was monitored by UV-vis spectroscopy Figure 3 shows the UV-vis spectra of the Sodium selenite solution incubated with leaf extract of *Manilkara zapota* as a function of time of reaction. The time at which the aliquots were removed for analysis is indicated next to respective curves. The characteristic SPR band occurs at ca.286 nm which was observed for 10 min and it later attained the maximum intensity after 24 hours. The yellow color solution changed into reddish orange colour which indicates the formation of selenium nanoparticles (Fig 2). The UV-vis spectra shows no evidence of absorption in the range of 200 to 500 nm for the plant extract and the plant extract solution exposed to Na_2SeO_3, ions shows a distinct absorption at around 286 nm which corresponds to SPR of selenium nanoparticles established (Mulvaney, 1996).

Fig.1 Photograph showing: (a) Aqueous extract of *Manilkara zapota* (b) sodium selenite solution (c) Selenium nanoparticles synthesized using *Manilkara zapota*

Fig. 2. UV-visible absorption spectrum of biosynthesized selenium nanoparticles using *Manilkara zapota*



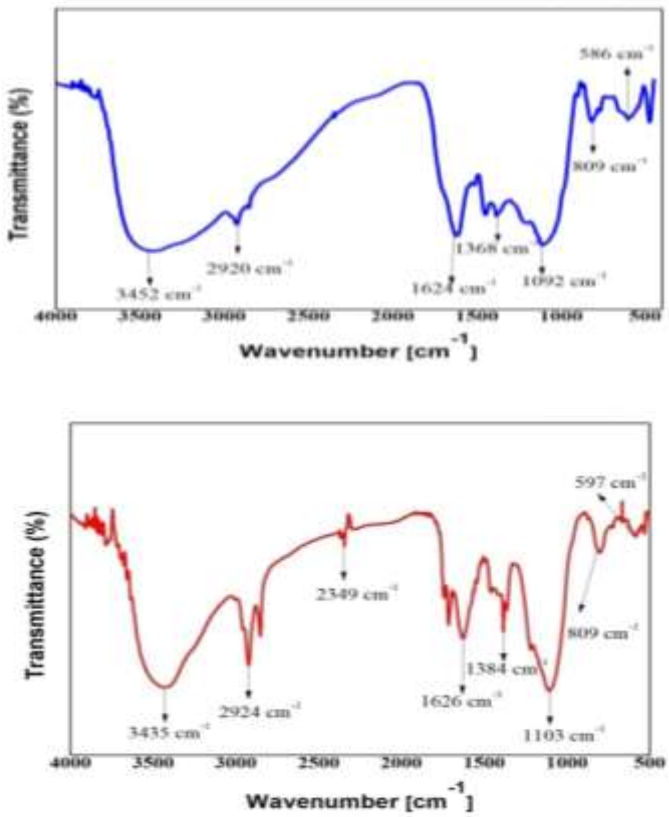
ISSN: 2278-4632
Vol-14, Issue-9, September: 2024

On comparing the bands it is clear that O-H stretch-alcohols and C-H stretch-alcohols, phenols and C-H stretch-alkanes are responsible for the reduction and capping of newly formed selenium nanoparticles (Figure 4 (A) and (B)).

The XRD pattern of newly synthesized selenium nanoparticles is shown in figure 5 the prominent peaks in the XRD spectrum were clearly noticeable. The peaks with 23.49, 29.81, 41.86, 43.78 and 51.71 correspond to crystalline planes of 100, 101, 110, 102 and 201 respectively. This pattern describes the amorphous nature of the selenium nanoparticle.

To find the morphology and size of the newly synthesized selenium nanoparticles, High Resolution Transmission Electron Microscopy (HR-TEM) analysis was undertaken. Then TEM images confirm the formation of selenium nanoparticles possess the fine geometric spherical, oval structure with regular contours (fig.). The diameter of newly formed selenium nanoparticles in located between 20-44 nm.

Fig.3 FTIR spectra of A. Leaf extract of *Manilkara zapota* B. Selenium nanoparticles synthesized by the reduction of aqueous sodium selenite using *Manilkara zapota.*



ISSN: 2278-4632
Vol-14, Issue-9, September: 2024

Fig.4. TEM micrograph of selenium nanoparticles newly fabricated using *Manilkara zapota*

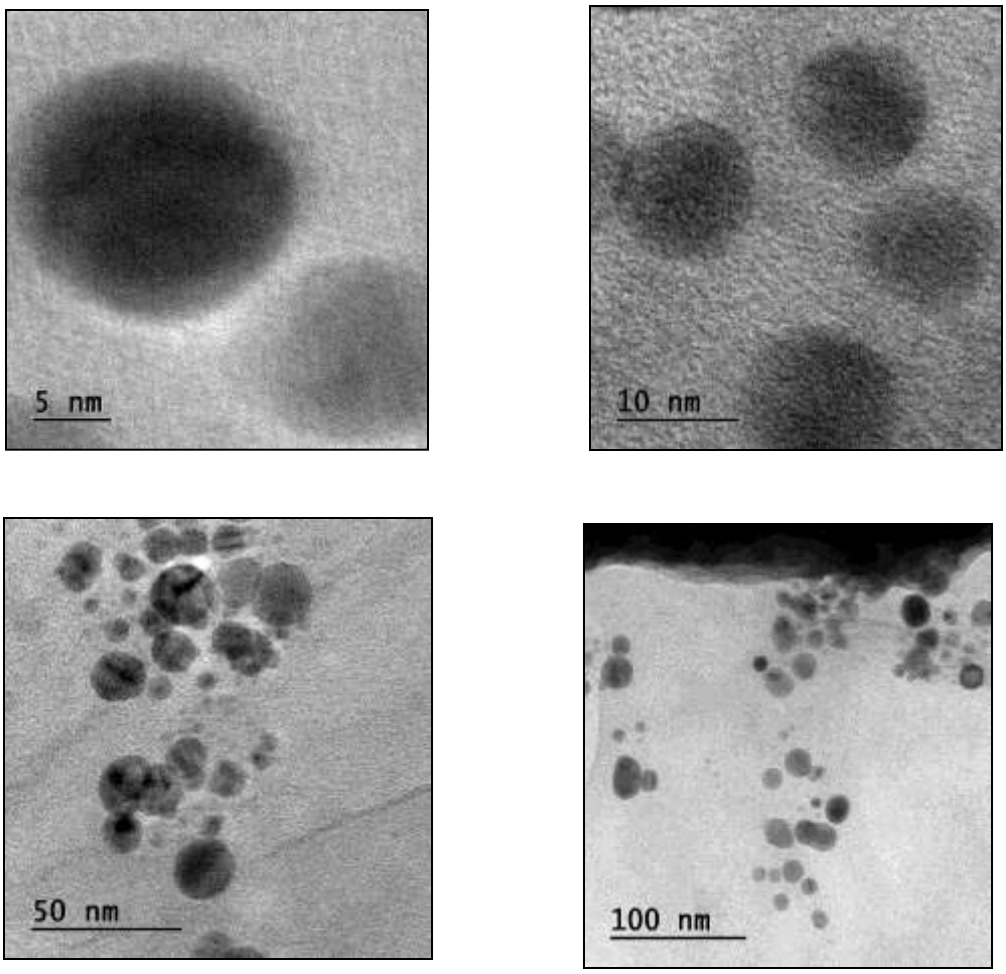
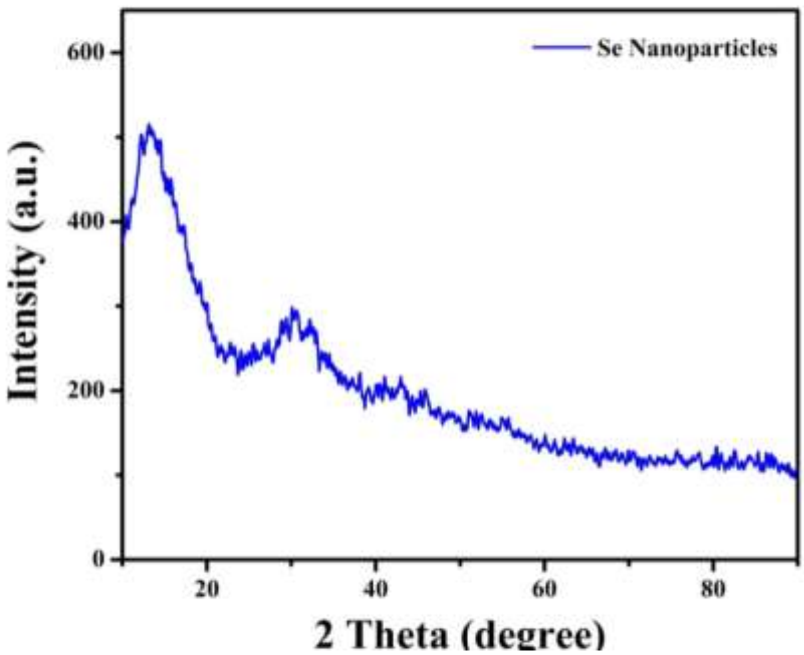


Fig.5. XRD patterns of selenium nanoparticles by *Malikara zapota*



ISSN: 2278-4632
Vol-14, Issue-9, September: 2024

4. Discussion

In the twenty-first century nanotechnology has become one of the most promising approaches for innovations that lead to fulfilment of the human needs. Research on the synthesis of nano-sized material is of great interest because of their unique properties like optoelectronic, magnetic, mechanical, photo responsive, catalytic properties(EL-sayed, 2001:Mc Connell, *et al*., 2000; Liu and Zhang 2001, Moreno-Manas and Pleixats 2003) and biomedical application (Lanone and Boczkowski 2006; Garnett and Kallinteri 2006) which differs from bulk. In nanotechnology, a particle is defined as a small object with size ranges between 1 and 100 that behaves as a whole unit in terms of its transport and properties. Nanonized materials have received great attention in the few years, due to the fact that they have different properties than their corresponding bulk or molecular counterparts.

Although so far several different techniques have been used in order to produce nonosized materials, for operational reasons, the most popular ones are the wet chemical process (co-precipitation, sol-gel and complexation). Other preparation techniques, involving physical vapour deposition (PVD), like sputtering, vapor phase diffusion and laser ablation (PLD), have distinct advantages over the chemical ones, since these often require a final calcination step, which makes them unsuitable for certain applications. Furthermore, with sputtering and laser ablation the stoichiometry of the material is maintained (Singh, *et al*., 1990). With PLD, the size of nanoclusters can be controlled by the laser parameters: power density, wavelength, pulse duration, and by the ambient gas conditions such as pressure, nature of the gas and flow rate. However, as it has been pointed out (Chen, *et al*., 1994), depending upon the ablated material, the size of particles is not always uniform and splashing is a common phenomenon in thin film deposition

The biological reduction of selenite leads to elemental red selenium is more insoluble and nontoxic (Dhanjal *et al*., 2010).On comparing the synthesis protocols inconcerned, with metal nanoparticles only limited work and techniques developed with respect to selenium nanoparticles. Certainly. among biological methods, the synthesis of selenium nanoparticles using plant powders and plant extracts from bark, leaves, seeds, pods and tuber have been actively pursued in the last few years. For example, single cell protein *Spirullina plantensis* (Yang, *et al*., 2012) and seaweed *Undaria pimatifalz* (Chen *et al*., 2006), *Vitis vinifera* (Sharma, *et al*, 2014), *Capsicum annum* (Li, *et al*., 2007). *Terminalia arjuna* (Prasad, *et al*., 2014) a). Fenugreek (Ramamurthy, *et al*., 2013). Lemon leaf (Prasad, *et al*., 2014b) and Broccoli (Kapur, *et al*., 2017) have been successfully used plant products to produce selenium nanoparticles with desired characteristics. In addition, studies have also proven that the plant extracts yield better results than the plant powders.

It is believed that a protective capping on biologically derived nanoparticles is mainly responsible for the toxicity variations. Many researchers have reported stabilization and capping of nanoparticles by binding with phenolics (Sharma *et al*., 2014), peptides/amines (Li *et al.,* 2007), hydroxyl/ketonic/carboxyl (Prasad *et al*., 2014a) present in the biological extracts of nanoparticles. Prasad and coworkers (2014b) confirmed the presence of partial deutriation of amine and hydroxyl/carboxyl in selenium nanoparticles synthesized using lemon leaf extract through FTIR. With the massive plant diversity much new plant species are in the way to be exploited and recounted in future era toward rapid and single step protocol with green principle.

The use of plant extracts for the synthesis of nanomaterials is cost competitive over the use of fungal and bacterial broth as it avoids the cost of microorganism isolation and culture media.

Results of the present investigation is one step synthesis and the resultant nanoparticles are stable. That there is no aggregation formed, nanoparticles are well dispersed. Ethnopharmacologically important functional molecules stabilization may provide medicinal value to the newly formed selenium nanoparticles. The versatility of nanoparticles in nano-based therapeutics, allows for a potentially wide variety of choices in the pay load, nanoparticles composition and targeting moietics. In current years nanomaterials-based medicines receives particular cconsideration as it holds the promise to revolutionize therapeutic treatment. The capability to produce three-dimensional multicomponent structure of nanoparticles also allow a great digree of flexibility to design drug delivery that may fulfill numerous desired properties akin to overcome the biological barriers, deliver hydrophobic, poorly water-soluble molecules and potential ability to route selected drugs to a preferred site in the body (Desai, 2012). The major advantages of nanoparticles over larger sized particles and its high surface to volume ratio and hence higher surface energy, unique optical (Kelly, *et al*., 2003) electronic and excellent magnetic properties (Predoi *et al*., 2003). The high surface area also allows it to modified adequately so as to improve its pharmacokinetic properties, increase vascular circulation life time, along with improving bioavailability, especially for biomedical applications.

5. Conclusion

The extracellular biosynthesis of the nanoparticles is economic compared to the intracellular method, because of the simplicity of the production process. The extracellular mode involves trapping the metal ions on the cell surface and reducing ions in the presence of enzymes. The sodium selenite

ISSN: 2278-4632
Vol-14, Issue-9, September: 2024

was reduced to selenium nanoparticles by using *Manilkara zapota* leaf extract. The formation of selenium nanoparticles (SeNPs) has been observed by the appearance of reddish orange colour. The biological reduction of selenite leads to elemental red selenium is more insoluble and nontoxic.On comparing the synthesis protocols inconcerned, with metal nanoparticles only limited work and techniques developed with respect to selenium nanoparticles.

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