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Phytochemical Mediated Synthesis of Goldnanoparticles

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ABSTRACT : *Synthesis of biocompatible nanomaterials, which can be used in the target drug delivery carriers, is a subject of interest in nanobiotechnology. Green chemistry approach for the synthesis of gold nanoparticles is being demonstrated using aqueous extract of seaweed, Sargassam ilicifolium. One step synthesis yields highly stable, monodisperse (spherical) gold nanoparticles in the size ranging from 2 to 30 nm. Characterization of newly formed goldnanoparticles was elucidated using, UV–spectral studies, Transmission Electron microscopic analysis, FTIR and XRD studies.*

KEYWORDS*: Sargassam ilicifolium, goldnanoparticles, TEM, UV Spectroscopy, X-ray diffraction.*

I. INTRODUCTION

Development of fuctionalized and hybrid gold nanomaterials play an indispensable role in overall design and development of Au nanomaterials - based nanopharmaceuticals. Recent interest in the development of novel strategies for the generation of gold nanoparticles stems from their significant applications in the wide spectrum of areas which includes nanomedicine. Application of colloidal nanomaterials appear to be fascinating in many industries including the pharmaceuticals, cosmetics, food, agriculture, health, environment and defense to name a few. The physicochemistry of nanomaterials are at the leading edge of the rapidly developing field of nanoscience. Due to a straight forward synthesis, stability and ease of incorporating functional groups for targeting capabilities, goldnanoparticles (AUNPs) have great application in pharmaceuticals, diagnostics and biosensors (Ghosh *et al*., 2008; Peng *et al*., 2009). The advantages of AUNPs come from their biocompatibility and ability to target delivery of therapeutic agent (Patra *et al*., 2008). The synthesis of goldnanoparticles normally involves a reduction of positively charged gold atom and an addition of stabilizing agents. In order to reduce the use of chemical and toxic waste to the environment, the synthesis of goldnanoparticles using natural compounds is of interest. The varieties of methods have been developed to achieve control over nanoparticles dimensions. Most of these methods are based on chemical reaction in solution (Suwicha soisuwan *et al*., 2010). Subsequently, strong interest is shown in the development of processes for such synthesis of nano gold particles with various shaped, sizes and surface chemistry (Gua *et al*., 2007; Singaravelu *et al* ., 2007).

Biological inspired experimental process for the synthesis of nanomaterials is one of the key issues in nanoscience research (Philip, 2010). Since the development of the concept of green nanomaterials, there has been a growing need for the biological and cytological compatible nanomaterials for application in medical a life sciences. The emergence of bioprocesses comes from nature through yeast (Ahmad *et al.,* 2003; Agnihotri *et al.,* 2009) fungi (Ingle *et al.,* 2008; Kathiresan *et al*., 2009; Ahmad *et al.,* 2003) bacteria (Nair and Pradeep *et al.,* 2002;; Nanda *et al.,* 2009) algae (Govindaraju *et al* 2009; Singaravelu *et al*., 2007; Govindaraju *et al.*, 2008) and plants (Shankar *et al.*, 2004; Singhal *et al.,* 2011; Sathyavathi *et al.,* 2010; Philip, 2011; Bankar *et al.*, 2010; Kora *et al.,* 2010) in the synthesis of environmental benign metal nanoparticles. This investigation involves the biological synthesis of goldnanoparticles using a seaweed possess several advantage. Through an elaborate screening involving number of seaweeds it is observed that *Sargassum ilicifolium* is a potential source for the synthesis of goldnanoparticles. Seaweeds are biological resources, present in many parts of world oceans. They are available largely in shallow coastal waters wherever there is a substratum on which they can grow and flourish. Seaweeds are the only source for the production of agar, alginate and carrageenam. Apart from these, seaweeds are extensively used for metal biosorption (Volesky and Schiewer, 1999). The metal biosorption potential of various brown, green and red seaweeds were evaluated by many investigators (Kuyucak and Volesky, 1989; Holan and Volesky, 1994). In general, brown seaweeds always performed well irrespective of metal ions employed. This is due to the presence of alginate, which is present in agal form in their cell walls (Volesky and Holan, 1995; Park et al., 2005). Thus, it is logical to investigate the possibility of the biosynthesis of goldnanoparticles by seaweeds. As a result seaweed *Sargassam ilicifolium* has been identified as a potential candidate for synthesizing goldnanoparticles.

II. MATERIALS AND METHODS

Seaweed (*Sargassum ilicifolium*) was collected from Mandapam Camp south east coast of Tamil Nadu, India. They were brought to the laboratory cleaned thoroughly in fresh water followed by distilled water and then shade dried for 3–5 days. Dried thalli were ground to powder in a glass mortar. 1 gm of biomass was kept in a 250 ml conical flask with 100 ml of deionized water for 24 hrs, after then extract was filtered. 10 ml of filtrate was added in 90 ml of 10^{-3} M aqueous $HAuCl_4$ solutions at room temperature. The bioreduction of Au^+ ions in aqueous solution was monitored by periodic sampling of aliquots (0.2 ml) of the suspension, then diluting the sample with 2 ml deionized water and subsequently measuring UV-Vis spectra of the resulting diluents. Material used for the synthesis of gold nanoparticles are chloroauric acid (HAuCl4) (Loba Chemicals).
The reduction of gold ions to gold nanoparticles was completed within 1 hour. The formation of ruby red coloured solution indicates the formation of gold nanoparticles. UV-vis spectrum was recorded as a function of time of reaction on a Techomp UV-2300 spectrophotometer operated at a resolution of 1 nm. The FTIR spectrum was recorded using Perkin-Elmer FTIR spectrophotometer. The seaweed synthesized gold nanoparticles solution was centrifuged at 10,000 g for 10 min. The deposited residue was dried and ground with KBr to obtain pellets for the purpose of FTIR analysis. X-ray diffraction pattern of dry nanoparticles powder was obtained using Siefert X-ray diffractometer operating at a voltage of 40 Kv and tube current of 30 mA with Cu-ka, radiation. High resolution transmission electron microscopic images were taken using a JEOL 3010 UHR TEM equipprd with a Gatan imaging filter.

III. RESULTS

On the technology front, large scale production of nanoparticles through green chemistry approach will eliminate chemical interventions, resulting in non-polluting industrial process, in the production of nanoparticles based smart materials. The present investigation addresses the production of gold nanoparticles using a seaweed aqueous extract. During the synthesis of gold nanoparticles with seaweed extract, a reaction mixture which was left at room temperature, turned in to ruby red colour after 1 h. UV-vis spectroscopic studies of the ruby red coloured solution confirmed the synthesis of gold nanoparticles as distinct SPR band with a sharp peak at around 529 nm.FTIR analysis has been carried out to identify the possible biomolecules responsible for the reduction of the Au^+ ions and capping the gold nanoparticles (Fig. curve 2a and 2b). Fig. 2A shows the FTIR spectra of aqueous extract of seaweed (*Sargassum ilicifolium*). Dry powder of, *S. ilicifolium,* where the strong bands were observed at 3432 cm^{-1} (H–bonded hydroxyl groups), 2925, 2854 cm^{-1} (–OH stretching), 1630 cm^{-1} (C–O stretching band of the carboxylic acid group), 1399, 1127 cm^{-1} (C–O stretching of alcoholic groups) (Fig curve a).The *S. ilicifolium* synthesized gold nanoparticles showed intense peaks at 3412, 2923, 2853, 1613, 1402, 1384, 1165, 1114 (Fig curve b). The peaks at 1127, 1399 (C–O stretching of alcoholic groups) are suppressed and the peaks at 1630 cm^{-1}, 3432 $cm^{-1}$are shifted to lower frequency [1613 cm^{-1}(C–O stretching band of the carboxylic acid group), 3412 cm^{-1} (H–bonded hydroxyl groups)] which indicates carboxyl group reduce gold ions into gold nanoparticles and hydroxyl group to stabilize nanoparticles surface (Fig. 2).

The XRD spectra of the newly synthesized gold nanoparticles are shown in Fig. 3. Three peaks were observed at 38.2^o, 44.3^o, 64.7^o and 77.5^o in the 2θ range 10^o-80^o which can be indexed to the (111), (200), (220) and (311) which is confirmed fcc structure of gold nanoparticles. The results reveal that the Au^+ reduced to Au^0 by *S. ilicifolium* are face centered cubic crystalline nature. TEM images obtained by the reaction of *S. ilicifolium* aqueous extract and 1 mM $HAuCl_4$ solution. The TEM microscopic images reveal the formation of monodisperse spherical gold nanoparticles with well dispersion. The obtained nanoparticles are quite uniform in size and in the range of 2 to 30 nm (Fig. 4). This study clearly demonstrates that *S. ilicifolium* works as the reducing and stabilizing agent simultaneously.

IV. DISCUSSION

Nanobiotechnology is a burgeoning interdisciplinary field of research interlacing material science, bionanoscience and technology. The advances made in the field of biotechnology and nanobiotechnology to harness the benefit of life sciences, health care and industrial biotechnology are remarkable (Stephen and Macnaughton, 1999; Gardea-Torresdey *et al*., 2002; Yeo *et al*., 2003). In recent times, there have been stupendous efforts for the development of efficient methodology for the synthesis of metal nanoparticles with unique exotic physicochemical and optoelectronic properties. The quest for cleaner methods of synthesis has led to the development of bio-inspired approaches. In the past decade, there have been increased interests on the biological syntheses of metal nanoparticles by bacteria, yeast, fungi, and plants (Shahverdi *et al*., 2007; Kowshik *et al*., 2003; Gajbhiye *et al*., 2009; Begum *et al*., 2009; Geetha *et al*., 2014).In recent years, various inorganic nanoparticles became subjects of significant interest in the view of their possible applications in the fields of engineering, and medicine. Monodisperse nanoparticles with selective shapes are important due to their potential applications in sensor technology, medical devices, optical devices, electronics, catalysis and biological labeling (Han *et al*., 2001; Rao and Cheetham, 2001; Moreno-Manas and Pleixats, 2003) which has been achieved in the present investigation. Plant extracts have been used as biological materials to synthesize nanoparticles particularly, to improve the monodispersity of nanoparticles and modulate their size and shape (Philip and Unni., 2011; Gardea-Torresdey *et al*., 2002). Among green synthesis methods, the use of plants for nanoparticles synthesis could be advantageous over other environmentally benign approaches like microorganisms–based technologies, as this eliminates the elaborate process of microorganism culture and the reaction time dramatically diminishes from several days to few hours. Among the metal nanoparticles gold nanoparticles have received major attention due to their unique and tunable surface plasmon resonance (SPR) (El-Sayed, 2001). Gold nanoparticles are the most commonly used nanomaterial in biosensing (Zheng *et al*., 2010; Hu *et al*., 2007; Amanda *et al*., 2005), biolabelling (Lin *et al*., 2009), delivering (Shih *et al*., 2009), photothermal therapy (Shakibaie *et al*., 2010), cancer therapy (Geetha *et al*., 2013; Ei-Sayed *et al*., 2005), imaging (Jain *et al*., 2008; Mohammed Fayaz *et al*., 2009), and catalysis (Alanazi *et al*., 2010) due to their unique properties of biocompatibility, oxidation resistance, optical absorption, fluorescence, Raman scattering, atomic and magnetic force and electrical conductivity. For each application, nanoparticles of different sizes and shapes are needed (Sun and Xia, 2002). In addition, functionalized gold nanoparticles play an indispensable role in the overall design and development of gold nanoparticles based pharmaceuticals (Basha *et al*., 2010).

As biological gold nanoparticles have no side effects in biomedical applications (Kaliappan and Viswanathan, 2008), the green chemistry approach for the synthesis of nanoparticles deserves merit. Based on the fact the present investigation gains their importance. Diverse pharmacological activities of seaweed have been well established. Seaweeds have caused an emerging interest in the biomedical area due to their content on pharmacologically bioactive substances with great changes to be employed against bacteria, viruses and other pathogens (Blunden, 1993; Ireland *et al*., 1993). Despite the ascending number of new findings about seaweed metabolites possessing biological activity on the last three decades few products having actual potential have been identified (Smit, 2004). Among those substances that received most attention from pharmaceutical companies for development of new drugs are the sulfated polysaccharides, the halogenated furanones and the kahalalide F (Smit, 2004). Polysaccharides represent a very interesting class of macromolecules, widely spread in nature and they have attracted more attention recently in the biochemical and medical areas due to their immunomodulatory effects (Ooi and Liu, 2000). In fact, seaweeds could be considered as a great source of polysaccharides, which have attained commercial significance due to their physical properties such as gelling, water-retention and their ability to emulsify (Moe *et al*., 1995; Smit, 2004).Indeed, it is expected that goldnanoparticles synthesized using the seaweed *Sargassam ilicifolium* might have medicinal properties. On the basis, efforts are being carried out to identify the medicinal value.

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Figure1. UV-vis spectra of *S. ilicifolium* synthesized gold nanoparticles

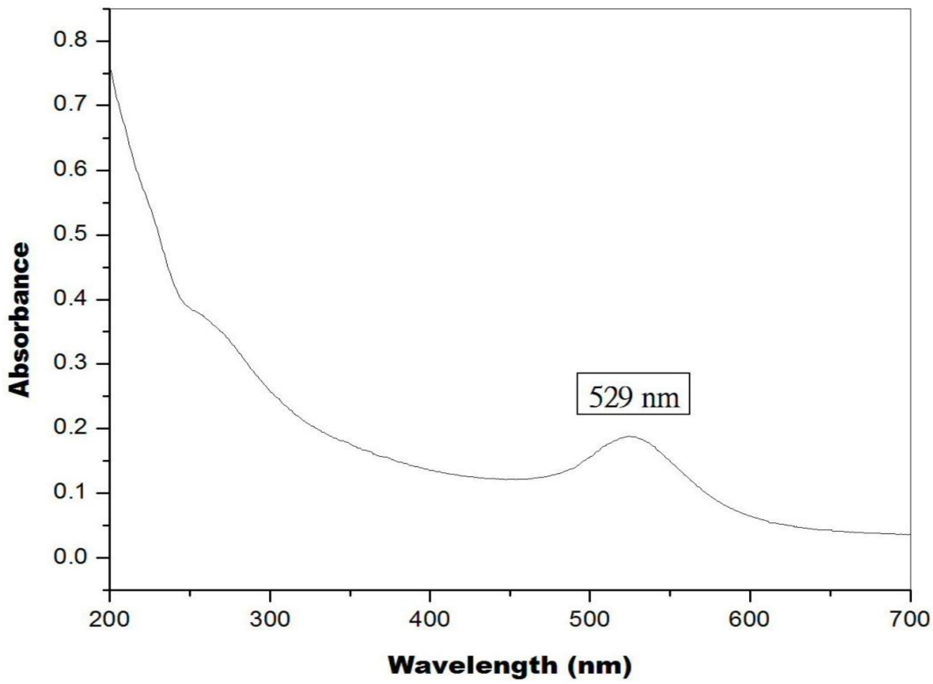

Figure 2. FTIR absorption spectrum obtained from (a). Aquoues extract of *S. ilicifolium.* (b). gold nanoparticles synthesized using *S. ilicifolium.*

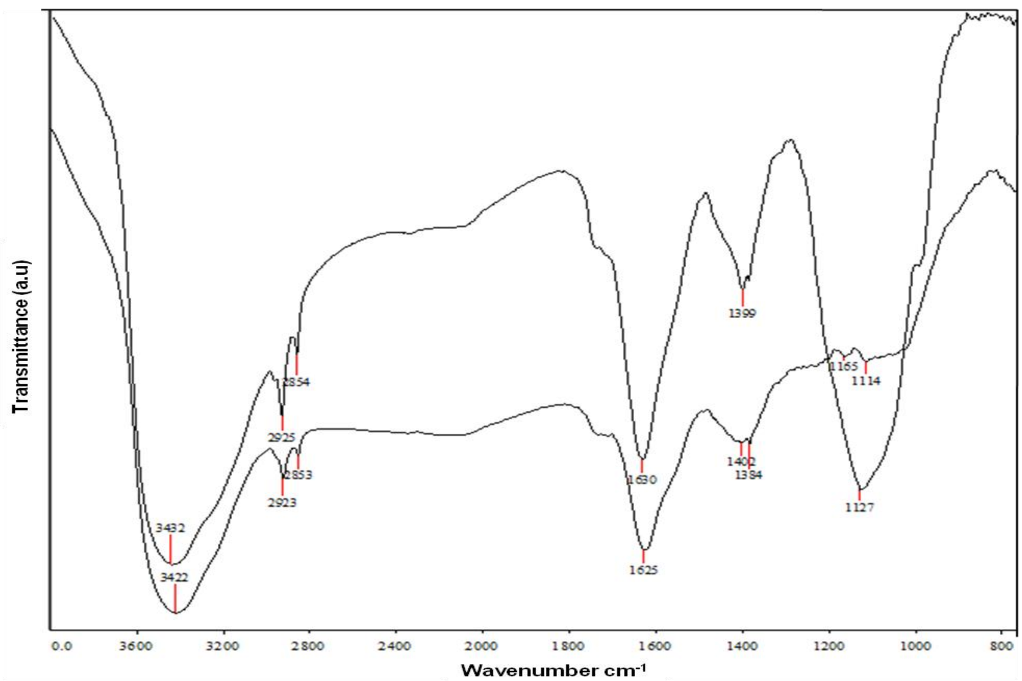

Fig.3. XRD pattern of gold nanoparticles synthesized using *S. ilicifolium*.

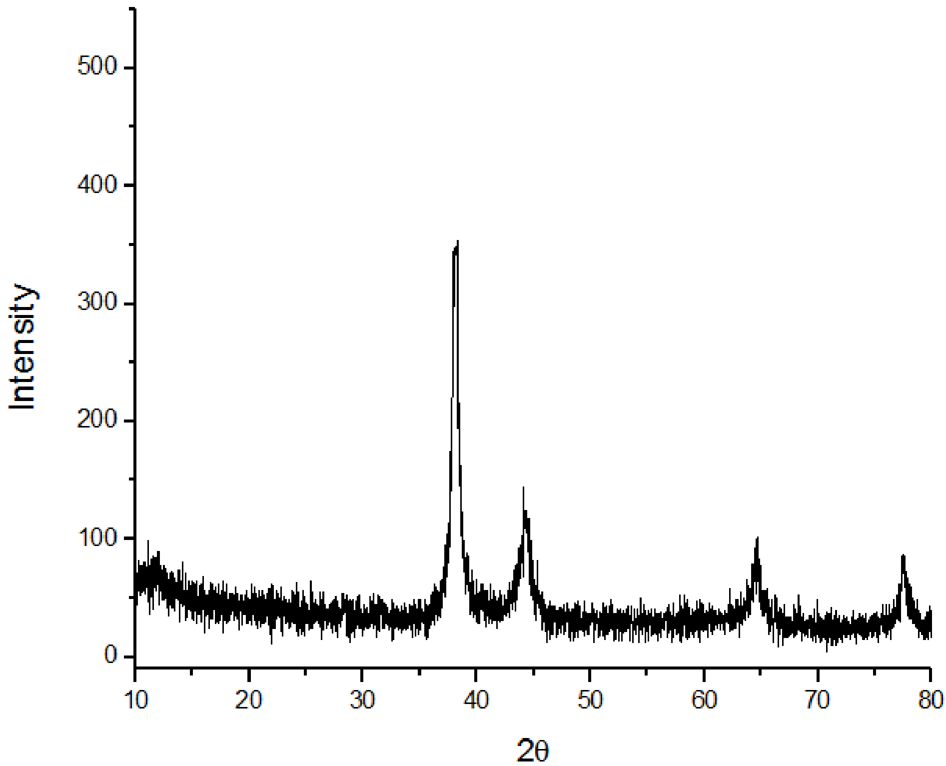

Figure 4.TEM image of gold nanoparticles synthesized *S. ilicifolium*.