

Biosynthesis and characterization of silver nanoparticles by using brown marine seaweed *Nizimuddiniazanardinii*

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In this study, the green synthesis of nanoparticles by using both fresh and dry marine macro alga of *Nizimuddiniazanardinii* was investigated. The Surface Plasmon Resonance bands of silver nanoparticles obtained were characterized by using UV-Vis spectrophotometer with characteristic absorption peaks at 413 and 414 nm. Maximum synthesis of silver nanoparticles was attained within 30 min at pH 8.5, 70°C and 1mM concentration of AgNO₃. Also maximum synthesis of silver nanoparticles reveals by characteristic absorption peaks at 432 and 441 nm within 2h at pH 7.5, 70°C and 1mM Ag₂SO₄. The SEM images demonstrated these nanoparticles as spherical structures with average size of 60 nm. EDX study showed the major signal of silver metal with concentration of 50.06% in the fresh seaweed. The structure of Ag-NPs was determined by X-ray diffraction (XRD). FTIR showed that the function groups of hydroxyl, carbonyl and amine compounds in *Nizimuddiniazanardinii* extracts were involved in the reduction of aqueous AgNO₃. This method of Ag-NPs synthesis is environmentally safe with potential utilization in biomedical and agriculture applications.

[**Keywords:** Green synthesis, Silver nanoparticles, *Nizimuddiniazanardinii*, SEM, XRD]

Introduction

Synthesis of nanomaterials has been investigated widely as these materials have unique broad range of optoelectronic and physiochemical properties in electronics¹, biosensors², catalyst material³, drug delivery system⁴ and magnetic⁵ applications. Excellent properties of nano particles are the result of crystallographic and morphological characteristics. They exhibit large surface area to volume ratio. This higher surface area to volume ratio leads to the change of the nano particles, properties better than the bulk particles⁶. The metallic nano particles are mostly prepared from metal substances such as Au, Pt, Pd and Ag synthesized by different physical, chemical and biological methods. Physically and chemically mediated syntheses need higher pressure, energy and temperature. Considerable cost and more toxicity are other disadvantages of physical and chemical methods⁷. Gerick and Pinches reported that size, shape and stability of the particles could be depended on various factors such as temperature, pH, time and substrate concentration⁸.

Among nanoparticles, silver nanoparticles have received major attention due to their unique and tunable Surface Plasmon Resonance (SPR) propriety⁹. Silver nano particles have many inhibitory effects in biomedical sciences and industrial processes^{10,11}. The

most important application of silver and silver nano particles is in medical industry to produce biosensors¹², antibacterial¹³, and anti-HIV¹⁴ drugs. Also topical antibiotics with the base of silver and silver nano particles are frequently prescribed for burn's and open wound's infections¹⁵.

For biological synthesis of silver nano particles bacteria¹⁶, fungi¹⁷, algae¹⁸, enzymes¹⁹ and plant extracts²⁰ can be used. Green synthesis of silver nano particles by algae extract provides more advantageous over other biological processes which use bacteria and fungi, because it eliminates the cell culture maintaining stage, and also it enables large scale production of silver nanoparticles²¹. This method is relatively easy to handle, safe, eco-friendly, low cost and has been well explored for the green synthesis of other nanomaterials²². Distinct advantages of Seaweeds are in their high metal uptake capacity, low cost and fast formation of Ag-NPs²³.

In this study, we investigated the formation of silver nanoparticles by the brown seaweed *Nizimuddiniazanardinii*.

Materials and Methods

Silver nitrate (AgNO₃) was purchased from Merck, Germany. Deionized water was used for all working and sample preparation. Samples of *Nizimuddiniazanardinii*

Seaweeds were collected by hand picking method from the intertidal zone of Oman's sea at southern coast of IRAN (Lat. 25° 17'N; Long. 60° 39'E). The seaweeds were washed thoroughly with tap water to remove inessential parts and then has been sent to the laboratory in an ice box. The cleaned samples of macro alga with deionized water were frozen and dried at -20°C and then grounded to a fine powder using kitchen blender and stored at 4°C. Dried and finely powdered *N. zanardinii* (10 g) was boiled with 100 ml of deionized water at 70°C for 20 min. The extract was filtered by using Whatman No.1 filter paper and used within a week at 4°C for further experiments.

In addition, fresh seaweed samples were washed thoroughly with tap water and then washed with deionized water for 5 min to remove extraneous materials. 50 g fresh *N. zanardinii* was boiled in 500 ml deionized water for 15 min. In next step the extract was filtered through mesh, followed by Millipore filter (0.45 µm), and then stored at 4°C for further studies.

20 ml of fresh and dry aqueous extract of seaweed was mixed with 100 ml AgNO₃ (1mM) solution in a 250ml Erlenmeyer flask. This reaction mixture was kept for the period of 2h, 24 h and 3day at 25°C and 70°C at the dark room under stirring condition (250 rpm). The pH of the reaction mixture was toward to the acidic pH (4.5) and alkali pH (8.5). Thereafter, the obtained solution was centrifuged at 12000 rpm for 10 min at the temperature of 4°C to get a clear solution of silver nanoparticles.

Photoluminescence spectra were carried out on UV-Visible spectrophotometer (Cary 100 cone Varian USA) Blanks for each set of sample set were only seaweed aqueous extracts. UV-Vis spectroscopy is a trustworthy method to study the presence of nanomaterials²⁴. Appearance of color rises from the property of the colored material to absorb selectively within the visible region of the electromagnetic spectrum²⁵. The presence of biomasses functional groups which are responsible for the reduction of silver ions were made in a Ker pellet. The spectra were recorded by using FTIR spectrometer (Thermo Nicolet, Nexus 870, USA FTIR) in the region of 400-4000 cm⁻¹ at a resolution of 4 cm⁻¹²⁶. The crystal nature and phase purity of the nanoparticles were determined by X-ray diffraction (XRD) patterns of silver nanoparticles. These pattern were recorded by STADI MP STOE diffractometer with Cu-Kα

radiation ($\lambda=1.5406 \text{ \AA}$) at a voltage of 40 kV and a current 30 mA²⁷. Scanning Electron Microscopy (Vega [XMU Tescam SEM) analysis were carried out to identify the morphology and size of the synthesized silver nanoparticles. Chemical composition of the products were determined by Energy dispersive X-ray (EDX) analysis which detected by secondary detectors at an operating voltage of 30 kV²⁸.

Results and Discussion

The biosynthesis of silver nanoparticles was proved by visual examination. Reduction of AgNO₃ in aqueous seaweed extract was visually evident by the color change (brownish-yellow) after 30 min of reaction (Fig. 1). The intensity of the brown color was directly related to the incubation period. Color change was due to excitation effect of Surface Plasmon Resonance (SPR) and reduction of AgNO₃²⁹.

The obtained silver nanoparticles were characterized by UV-Visible spectroscopy at the absorption range of 400-450 nm³⁰. Characteristic absorption peaks at 413 and 414 nm for fresh and dried *N. zanardinii* in the spectrum confirmed of Ag-NPs (Fig. 2)³¹. According to our findings, the fresh extract has more potential for the synthesis of nanoparticles compared to the dried extract. We found out that, the color intensity at 413 nm increases with the length of time (Fig. 3). This is similar to the characteristic peaks of silver nanoparticles that prepared by chemical reduction method^{32,33}.

The potential and morphology of nanoparticles depend on the pH of solution. Color changes were happened at pH 4.5 in 50 min and at pH 8.5 in 25



Fig. 1 — The aqueous extract of *N.zanardinii*(A) before; and (B) color change after synthesis of Ag-NPs

min. At lower pH, accumulation happened due to the over nucleation and formation of large nanoparticles. At higher pH, a large number of nanoparticles with the small surface area were present due to the bioavailability of functional groups in the seaweed

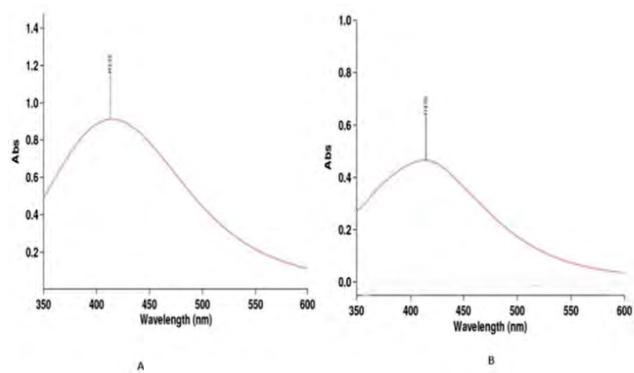


Fig. 2 — UV absorbance of silver nanoparticles synthesised by A) fresh and B) dried *N.zanardinii* extract

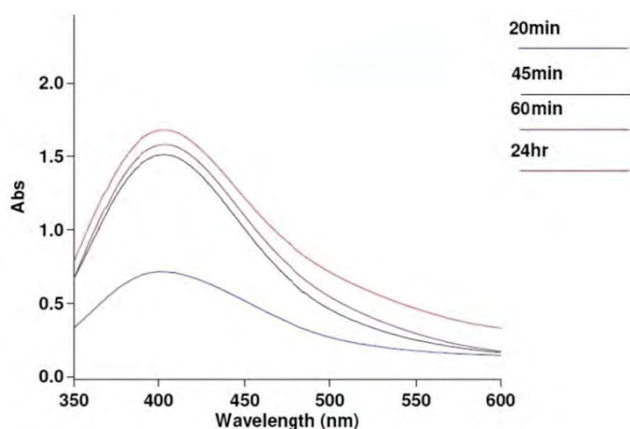


Fig. 3 —UV-Visible absorption spectra of silver nanoparticles with different time intervals

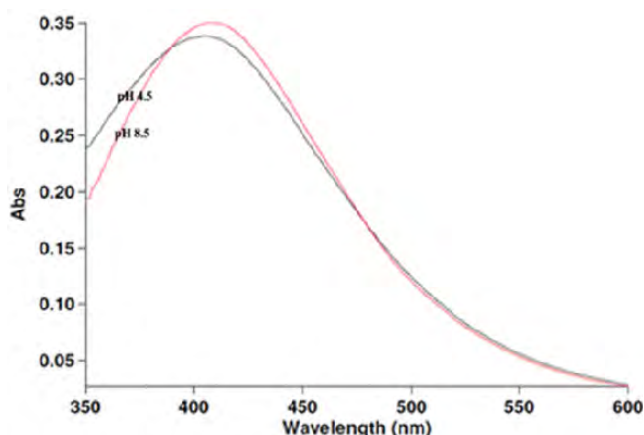


Fig. 4 — Effect of reaction pH on the production of silver nanoparticles

extract³⁴. The pH of 8.5 was optimum for the Ag-NPs formation (Fig. 4). The pH plays an important role in controlling shape and size of Ag-NPs that previously reported in³⁵.

Another important parameter was temperature, which studied at 25°C, and 70°C (Fig. 5). This figure shows that the intensity absorption peak increases as temperature rises from 25°C to 70°C and broadening peak in the absorbance band appears at 420nm wavelength area. Rate of silver nanoparticles formation was increased rapidly when temperature raised because in higher temperature, the reduction happened very hastily³⁶.

The obtained nanoparticles were characterized by UV-Vis spectroscopy (Fig. 6). This figure shows that the maximum synthesis of silver nanoparticles was attained within 2h and at 70°C, with 1 mM Ag₂SO₄. For the first time, this investigation showed that for silver nanoparticles formation, silver sulfate solution can be used instead of silver nitrate solution.

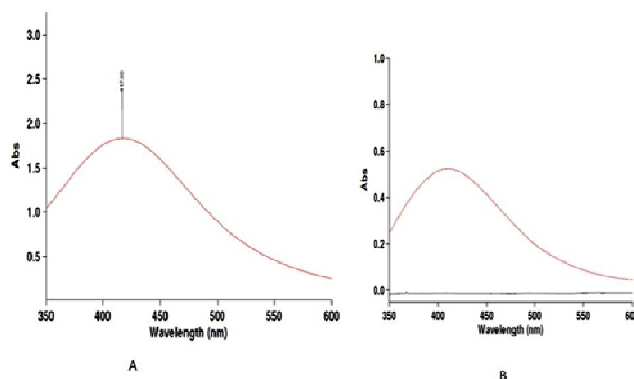


Fig. 5 — UV absorbance of silver nanoparticles after 1h of reaction at different temperature: A) 70°C and B) 25°C

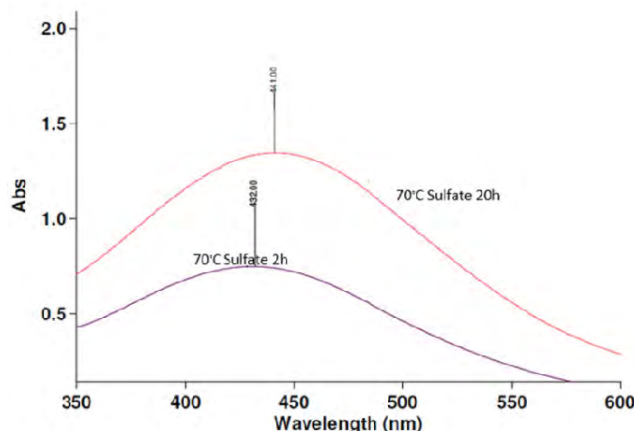


Fig. 6 — UV spectrophotometry of aqueous solution of 1mM Ag₂SO₄ with *N.zanardinii* extract

FTIR evaluates the existence of different functional groups of biomolecules, which are responsible for the transformation of AgNO_3 bio-reduction into Ag-NPs³⁷. The FTIR spectra were carried out for both *N. zanzardinii* and synthesized silver nanoparticles. Figure 7 shows the spectra of seaweed aqueous extract and silver nanoparticles AgNPs.

Figure 7A represents the FTIR spectrum of *N. zanzardinii* extract, which peaks at 879, 1077, 1670, 2890 and 3429 cm^{-1} . Two peaks at 3429 cm^{-1} (O-H stretching) and 2890 cm^{-1} (CH stretching) were also detected. In addition, the peak at 1077 cm^{-1} indicated C-O band that verification involved O-H group³⁸. The peak at 1670 cm^{-1} showed C = O stretch α , β -unsaturated aldehydes, and ketones³⁹. The observed bands at 879, 624 are due to C-Cl and C-Br of alkyl halides⁴⁰.

The FTIR spectrum analysis discloses the functional groups of the silver nanoparticles synthesized with *N. zanzardinii* extract and shows different bands at 3445, 2926, 2356, 1647, 1460, 1082, 878, and 629 cm^{-1} (Fig 7B).

The band at 3445 cm^{-1} is the characteristic of the hydroxyl groups⁴¹, H-bonded alcohols, phenols, or N-H stretching of 1° and 2° amines and amides⁴². The shifting of the band from 3429 to 3445 cm^{-1} are due to hydroxyl groups which reduce Ag^+ to Ag. There is a shift in the absorption band of 1670-1647 cm^{-1} . The

shifting of the band from 1670 to 1647 cm^{-1} may be due to the binding of (NH) C=O group in nanoparticles⁴³. The band 1082 cm^{-1} shows C-O stretch alcohols and carboxylic acid, which disappeared after synthesis of Ag-NPs. Thus, the amine, peptide and proteins groups may play an important role in the reduction of AgNO_3 into Ag nanoparticles. The above-mentioned shift was also observed in *Padinatetrahromatica*⁴⁴.

The X-ray diffraction study was carried out to confirm the crystalline nature of synthesized silver nanoparticles. The diffraction peak at $2\theta = 46^\circ$, 64° and 78° , with those reported for the structure of standard silver metal (Ag°) (Fig. 8). In addition,

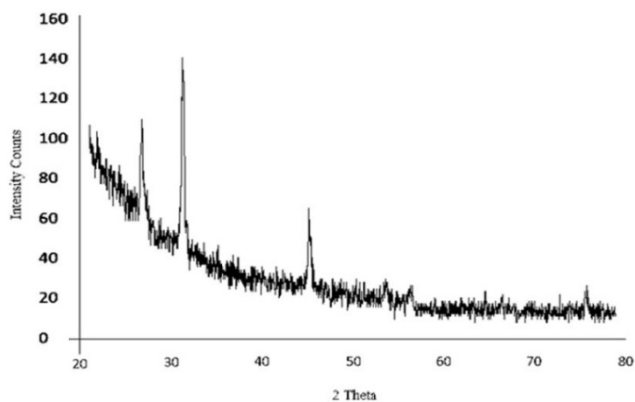


Fig. 8 — XRD analysis of synthesised silver nanoparticles

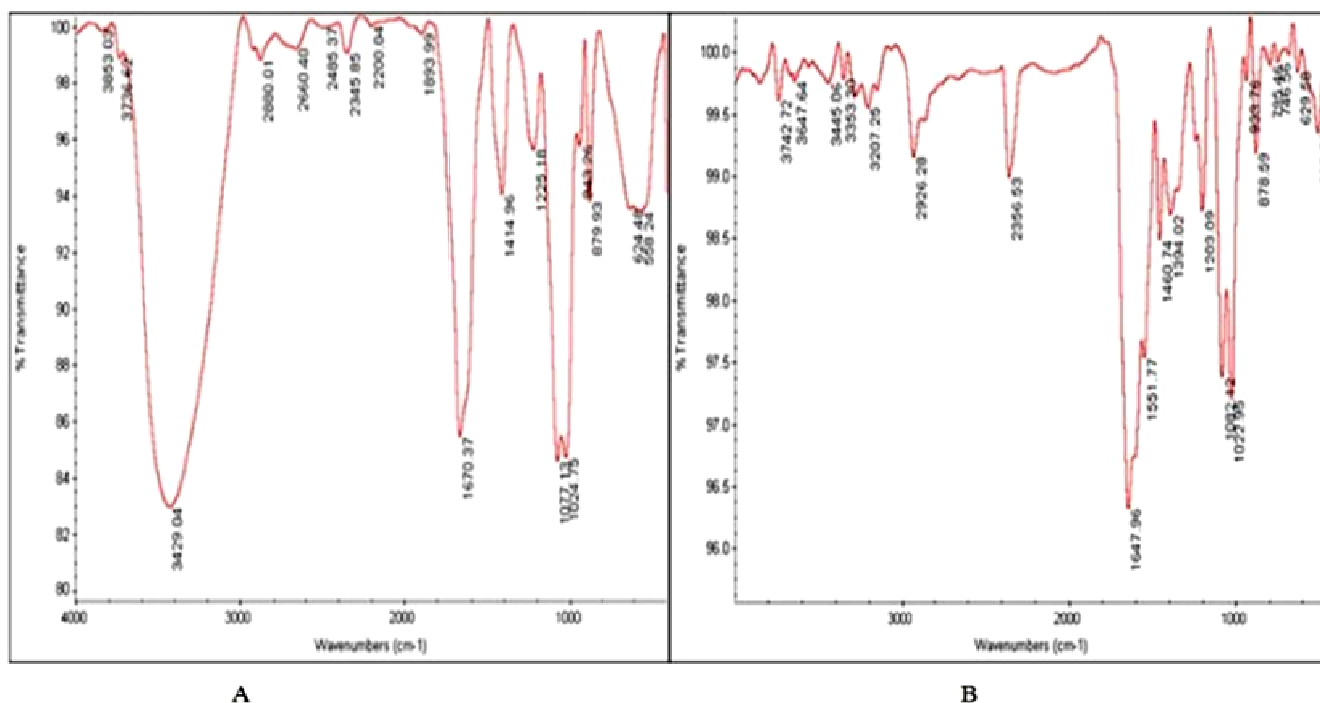


Fig. 7 — FTIR spectrum for (A) the *N.zanzardinii* aqueous extract, and (B) *N.zanzardinii* formed AgNPs

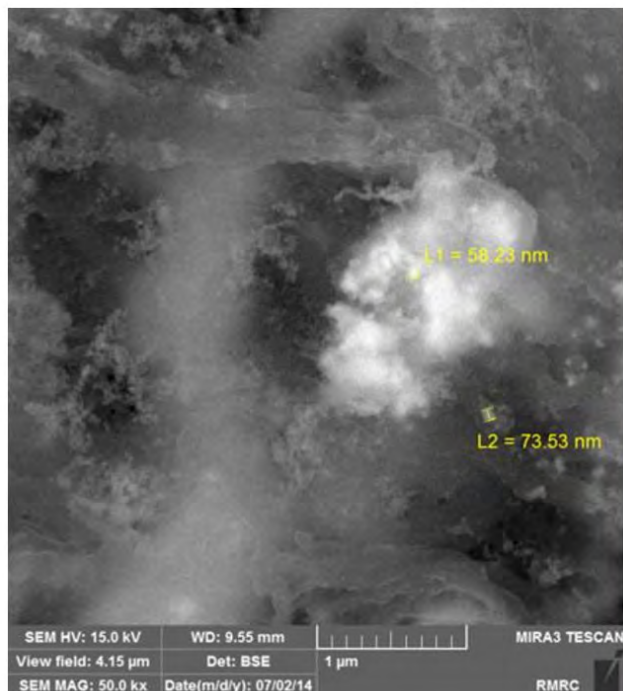


Fig. 9 — SEM image of AgNPs synthesised using extract of *N. zanardinii*

some peaks were seen at 27.7°, 33°, 54° and 56°, which these peaks might be the result of bio-organic compounds proteins in the nanoparticles during the synthesis [45]. The formation of Ag₂O may be due to the coupling reaction with (O-H) groups. This result is similar to the Kumar et al. study [46]. The size of formed silver nanoparticles in the bio reduction process can be determined by using Debye-Scherrer's equation.

Scanning Electron Microscopy (SEM) image shows the morphology of silver nanoparticles. The Figure 9 shows the morphological characteristics of silver nanoparticles synthesized by the extract of *N. zanardinii*. This image shows the magnified view of macro alga assisted silver nanoparticles as spherical shapes and the average size of 60nm. The SEM analysis for silver nanoparticles of *N. zanardinii* is similar to the results of silver nanoparticles synthesized from the *Turbinariaconoides* seaweed.

Energy dispersive X-ray spectroscopy (EDX) reveals the chemical features of synthesized nanoparticles derived from *N. zanardinii* extract (Fig. 10). The strong signal was detected at 3 eV confirming the presence of silver elements in nanoparticles due to Surface Plasmon Resonance. There were also some weak signals from N, K, Ca and Cl in the EDX data.

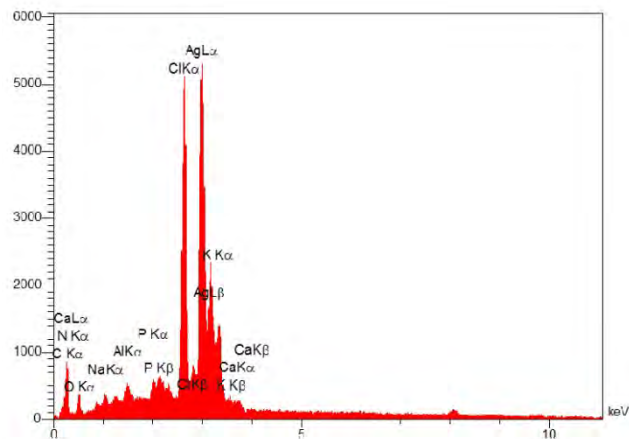


Fig. 10 — EDX spectrum of synthesised by using the *N. zanardinii* extract

Conclusion

This research is the first green synthesis of silver nanoparticles from *N. zanardinii*. In this biosynthesis process, nanoparticles were formed within 20h at 25°C and 30 min at 70°C. The maximum absorbance was observed at 417 nm. Our research showed that by increasing pH, synthesis of Ag-NPs increases and also the fresh extract has more potential for the synthesis of nanoparticles compared to the dried extract. In addition, in this research silver sulfate solution was used for the first time in the biosynthesis process within 2h at 70°C with 1mM silver sulfate solution. This method of Ag-NPs synthesis does not produce any toxic reagents and thus could be useful in biomedical and agricultural applications.

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