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Green Synthesis And Characterization Of Copper Oxide Nanoparticles Using A Red Seaweed Gracilaria Edulis

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Abstract: *This work represents a novel and eco-friendly method for synthesizing copper oxide nanoparticles from a red seaweed- Gracilaria edulis. The method used for synthesizing nanoparticles was sol-gel method. Seaweed was collected from Rameshwaram, with the help of local fishermen and identified using keys available. Morphological criteria of Seaweeds were confirmed at the Regional Center of CMFRI, Mandapam Camp, Tamil Nadu.. The synthesized nanoparticles were characterized using UV spectroscopy showed a surface plasmon peak at 410 nm, which is characteristic peak of Copper oxide nanoparticles.Using energy dispersive X-ray spectrometry (EDX) analysis, a distinct peak of CuO was confirmed. Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and UV-visible absorption spectroscopy confirmed the reduction of Copper oxide nanoparticles. The complete reduction of metal ion was attained within 5 hours of time span. This is the first study on synthesis of copper nanoparticles using a red seaweed.*

Keywords **-** *Gracilaria edulis – red seaweed, Copper oxide nanoparticles, Green synthesis, Optical characterization.*

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I. INTRODUCTION

Nanomaterials of various shapes and sizes have been thesubject of utmost interest due to their potential applicationsin industries, biomedical diagnostics, environmental remediation and electronics,over the past decade. At present, biological methods have an increasing interestbecause of the necessity to develop new clean, cost-effectiveand efficient synthesis techniques.The metallic nanoparticles are most promising and remarkable biomedical agents. Due to their large surface volume ratio, they govern interest of researchers. Among the developed nanoparticles, copper nanoparticles are pertaining to have a wide range of application in the fields of physical, chemical, various solution of environmental issues and biological science[1]. It is a method to produce solid materials from small molecules. This method is also used for the fabrication of metal oxides, chiefly the oxides of titanium and copper. The process includes conversion of monomers into a colloidal solution that acts as the precursor for the gel of either discrete particles or network polymers. Metal oxides are taken as a typical precursor[2].

Algae are also used as "bio-factories" for synthesis of metallic nanoparticles. Among different genera of bioreductants, seaweeds have distinct advantages due to their high metal uptake capacity and low cost. Rapid synthesis of copper nanoparticles through extracellular biosynthesis from seaweeds is feasible. The genus Gracilaria edulis comprises intertidal and subtidal red seaweeds and encompasses about 130 species, that are widely distributed and are available throughout the year. The highest species diversity is in subtropical regions[3]. No work has been done on any of the red seaweeds for the synthesis of Copper oxide nanoparticles. This motivated the present investigation on the synthesis of CuONPs using Gracilaria edulis seaweed.

Copper (II) oxide or cupric oxide is the inorganic compound with the formula CuO. A black solid, it is one of the two stable oxides of copper, the other being Cu_2O. As a mineral, it is known as tenorite and paramelaconite. It is a product of copper mining and the precursor to many other copper-containing products and chemical compounds[4]. It is produced on a large scale by pyrometallurgy used to extract copper from ores. The ores are treated with an aqueous mixture of ammonium carbonate, ammonia, and oxygen to give copper(I) and copper (II) ammine complexes, which are extracted from the solids. These complexes are decomposed with steam to give CuO.Copper oxide nanoparticles green synthesis plays a role in photocatalytic dye degradation. The enormous volume of environmental pollutants, nondegradable and carcinogenic nature coloured dye effluents is discharged by the textile and paper industries. Moreover, to unique in their products, most of the industry uses colour dyes, without any treatment of colouring materials are liquidated in water leads to contamination of resources. Nowadays, a photocatalytic method got the wide attention due to its effective decolorization of dyes [5].

II. Materials And Methods

Gracilaria Edulis.-The Chosen Seaweed For The Study

2.1 Collection and Identification

Seaweed Gracilaria edulis were collected from intertidal rocky shore regions in Mandapam, Gulf of Mannar region, India and identified using keys available (Ganesapandian and Kumaraguru 2008). Morphological criteria of Seaweeds were confirmed at the Regional Center of CMFRI, Mandapam Camp, Tamil Nadu. Samples were rinsed with sea water to remove debris and epiphytes. The epiphytes were removed using soft brush. In the laboratory, the seaweeds were once again washed in freshwater and deionized water for the removal of salt, sand and then shade dried. After complete drying, for 5 days at room temperature, samples were cut into small pieces.

2.2 Preparation of the Seaweed extracts

For preparation of extracellular synthesis 10g seaweed leaf was taken with 100ml of distilled water and kept in a water bath for 10min at 70^0C. The extract was filtered through Whatman No.1 filter paper (Millipore Millex) and the filtrate was collected in a 250-ml Erlenmeyer flask and stored in a refrigerator at 4qC for further use. This process was repeated for each seaweed sample separately to collect the filtrate.

2.3 Biosynthesis of Copper oxide nanoparticles

To about 5ml of copper solution were added to 5 ml of seaweed leaf extract. The pH of the solution was controlled by buffer solution (1M NaOH, 1M HCl), fixing the values at 5, 7, and 10 with continued stirring. After the black precipitate was formed, the prepared emulsion was placed on a magnetic stirrer and stirred for 1hr at room temperature[6].

2.4 Purification of nanoparticles

To remove the non-metal components along with maximal recovery of metal nanoparticles from the synthesized solution, an optimal centrifugation process was obtained based on tests of two centrifugation forces 12,000 and 15000 rpm for 30 min. Biosynthesized metal particles in aqueous upper layer were collected. Collected layer of solution was redispersed in sterile deionized water to get rid of any biological molecules. The process of centrifugation and redispersion in sterile deionized water was repeated thrice to obtain better separation of entities from the metal nanoparticles. The centrifugation process was done using a refrigerated centrifuge (REMI, India)[7].

2.5 Characterization of metal nanoparticles

The synthesized nanoparticles were characterized by various techniques viz., UV-Vis Spectroscopy analysis, Fourier transform Scanning Electron microscopy (FESEM) and Energy dispersive X-ray analysis (EDAX), X-ray diffraction analysis (XRD) which provide important information for the understanding of different physicochemical features.

2.6 UV-Vis Spectroscopy analysis

Ultraviolet-Visible spectrophotometer is designed to use light of ultraviolet and visible spectral region. This technique is used to determine the concentrations of unknown solutions and determination of transition metals whose electron transition energy that falls under UV or visible regions. Beer-Lambert law is used to determine the concentration of unknown solutions. It states that the absorbance of light of a material is directly proportional to the concentration of material in solution and the path length of solution through which the light passes. The blue shift in the absorption peak denotes decrease in the particle size.

2.7 FESEM and Energy dispersive X-ray (EDAX) analysis

The Fourier transform scanning electron microscope uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. Scanning Electron Microscope is used to image and analyze materials of sizes that are less than a micrometer in range. The electrons are accelerated by the potential difference between cathode and anode. The electrons emitted are secondary electrons, back scattered electrons and auger electrons which decide upon the energy spectrum that is available by the interaction of electrons and specimen.

2.8 X-ray diffraction (XRD) Analysis

X-ray diffraction is a versatile, non-destructive analytical method for identification and quantitative determination of various crystalline forms, known as 'phases' of compound present in powder and solid samples. Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. The phenomenon is common in the natural world, and occurs across a broad range of scales. XRD is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. When a monochromatic X-ray beam with wavelength lambda is projected onto a crystalline material at an angle theta, diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number n of wavelengths. From XRD, the crystallite size (t) of the particles can be found out by using the Scherrer's formula.

III. Results And Discussion

3.1 Characterization Analysis

Reduction to copper oxide from the seaweed extract could be followedby colour change from red to black precipitate (Figure 1) andfurther by UV-vis spectroscopy. The peak observed at 280 nm confirmed the synthesis of CuONPs as it agrees with the previous reports [8]. Though initiallythere was no significant peak at 2 min but at 4 min thebuilding of peak at 280 nm marked the initiation of synthesisof CuONPs. Subsequent rise in peak with a maximumat 20 min supported that the reported route of CuONPssynthesis is novel as well as rapid as compared to Mirabilis jalapa flower wherein the synthesis was reported to becompleted in 2 h . Similarly, it was found to be fastereven as compared to black tea extract [9]. Optimizationstudies showed that 0.7 mM facilitatedmaximum synthesis of CuONPs as compared to other concentrations. Synthesis failed to be initiated at lower temperatures like 4and 20°C while a moderate rate of reaction was observedat 30 and 40°C. The rate of reaction was found to be maximumat 50°C which supported the fact that highertemperature plays a key role in enhancing the reaction ratewhich is in well agreement with synthesis of CuONPsmediated by Nyctanthesarbortristis flower extract[10.]

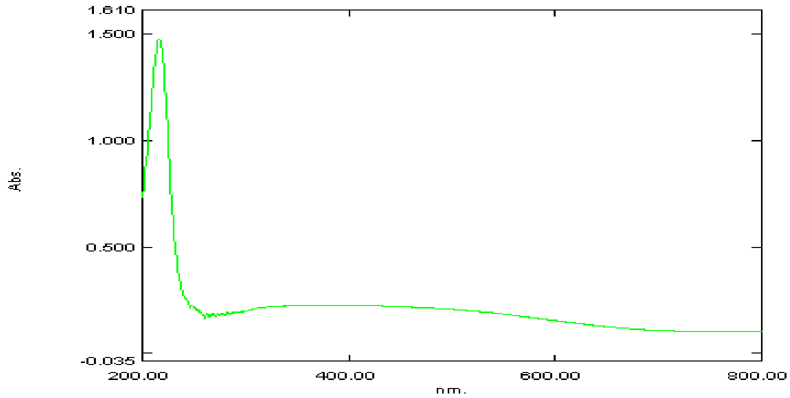

Figure 1 UV vis spectroscopic analysis of copper oxide nanoparticles from gracilaria edulis

The phase formation of the synthesized CuONPs was analysedemploying X-ray diffraction which confirmed thatthe bioreduced metal nanoparticles are of copper oxide nanoparticles (Figure 2). Existance of peaks (110), (100), (002),(101),(102), (110) (200), (201), (004), (202) and (311)matched with the standard Joint Committee for PowderDiffraction Set(JCPDS) data. This confirmed facecentered cubic structured AuNPs formation. Peak broadeningindicated restricted particle size. Enlarged pattern of(101) peak is shown in the inset of XRD plot. The crystallitesize was calculated using Scherrer's formulaHere 0.9 is the shape factor, generally taken for a cubic system,λ is the x-ray wavelength, typically 1.54 Å, β is the fullwidth at half the maximum intensity (FWHM) in radians,and θ is the Bragg angle. Using the above formula the crystallitesize calculated is ~10 nm.

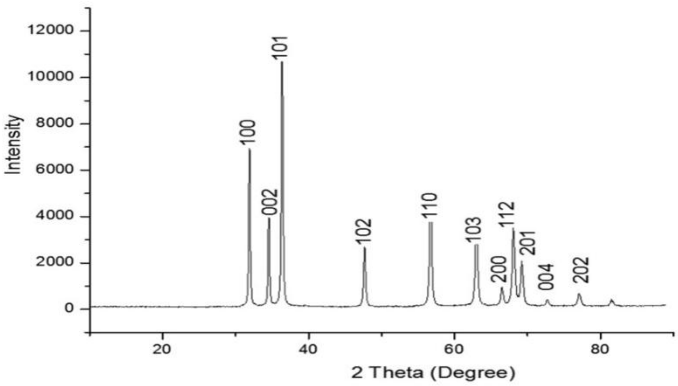

Figure 2 XRD analysis of copper oxide nanoparticles from gracilaria edulis

A strong clear peak for copper oxide atoms was seen in the spotdirectedEDX spectrum of all the CuONPs (of Fig. 3).The presence of carbon, nitrogen and oxygen atoms was indicated by the weaker signals. This is likely to be due to X-rayemission from proteins/enzymes present in the biomoleculesthat had capped the Copper oxide nanoparticles. Given that the CuONPs hadremained stable (retaining clear shapes) even after the pistiaextract had been centrifuged out, these signals can only befrom biomolecules that have remained adhered to the CuONPs.An optical absorption peak at approximately 2 keV is seen,which is characteristic of Copper nanoparticles. Copper 78.46 % and Oxygen 21.54 % strong signal is formed which indicate CuO NPs formation

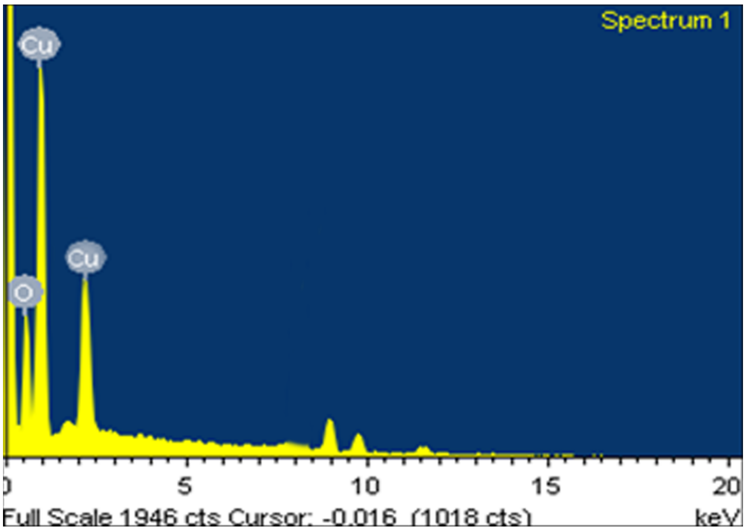

Figure 3 EDX analysis of copper oxide nanoparticles from gracilaria edulis

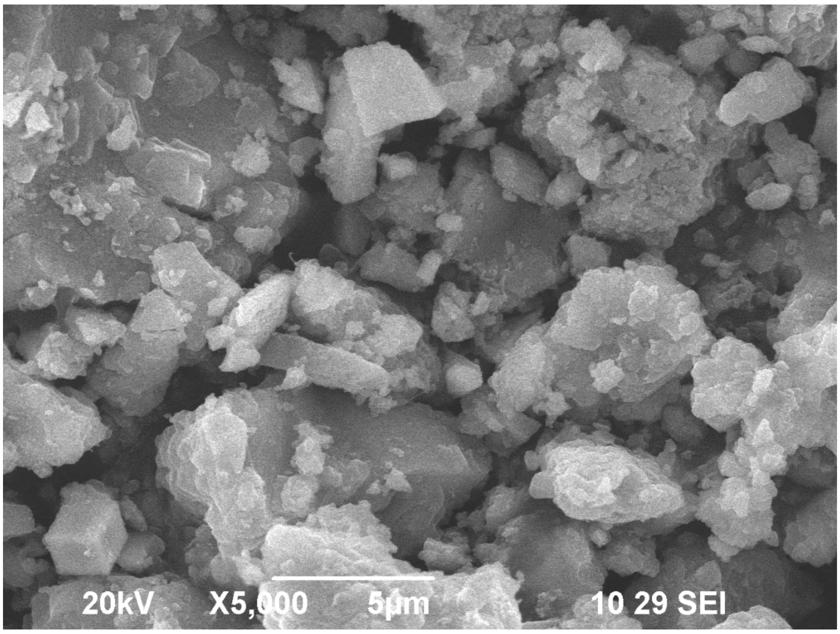

Figure 4 FESEM analysis of copper oxide nanoparticles from gracilaria edulis

The surface morphology and size of the nanoparticles were obtained by Scanning Electron Microscopy (SEM) analysis. The Fig. 4 shows the CuONPs synthesized by the plant extract of Gracilaria edulis. The electrostatic interactions and hydrogen bond between the bio-organic capping molecules bond are responsible for the synthesis of copper nano particles using plant extract. It was shown that spherical and relatively uniform shape of the copper nanoparticles was confirmed in the range of 60-100nm. The quantitative and qualitative analysis of elements may be concerned in the formation of copper nanoparticles. They were identified by EDAX analysis (Fig.4).Due to the Surface Plasmon Resonance, the copper nanoparticle shows the absorption peaks of higher counts

IV. Conclusion

In conclusion Gracilaria edulis mediated synthesis of CuONPs has been demonstrated to be a rapid and environmentally benign route. Variation of reaction conditions had pronounced effect on the reaction on various environmental activities which are proposed as future studies. CuONPs with shapes of spherical was synthesized. Spherical nanoparticles were in abundance which were found to be face centered cubic (FCC) structuredgold (111). BioreducedCuONPs showed excellent catalytic properties in a reduction reaction of 4-nitrophenol to4-aminophenol by NaBH4 in aqueous phase. Thus, bringing into light yet another use of the seaweed ,besides its usual utilities. The method stands out primarily due to the fact that it is eco-friendly and shuts down the demerits of conventional physical and chemical methods. The particles obtained showed characteristic results for the various characterization techniques carried out thereby confirming its elemental and structural natures as well as crystallinity .The present report emphasizes that seaweed extracts can be cost-effective precursors for largescale preparation of CuONPs, which can be used as an environment-friendly and economically viable photo catalysts for wastewater treatment.

Conflict Of Intrest

The authors do not have any conflict of intrests.

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