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Short communication

Photocatalytic degradation of methyl orange dye using silver (Ag) nanoparticles synthesized from *Ulva lactuca*

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ABSTRACT

In this paper, we report on biosynthesis of silver nanoparticles using *Ulva lactuca* (seaweed) at room temperature along with photocatalytic degradation of methyl orange dye. UV spectral analysis showed peak at 430 nm with special reference to the excitation of surfaces plasmon vibration by silver nanoparticles. FT-IR studies reveal the presence of bioactive functional groups such as phenolic compounds, amines and aromatic ring are found to be the capping and stabilizing agents of nanoparticles. The morphology of silver nanoparticles was found to be spherical and ranges about 48.59 nm as confirmed by HR-SEM. Negative zeta potential value of −34 mV suggests that the nanoparticles are highly stable in colloidal solution. XRD patterns also suggest the occurrence of spherical shaped particles due to the presence of silver ions. Further, photocatalytic degradation of methyl orange was measured spectrophotometrically by using silver as nanocatalyst under visible light illumination. The results revealed that biosynthesized silver nanoparticles using *U. lactuca* was found to be impressive in degrading methyl orange.

1. Introduction

Dyes belong to the class of synthetic organic compounds and are widely used in the textile industry. The removal of these non-biodegradable organic chemicals from the environment is a crucial ecological problem. Many techniques, such as activated carbon sorption, flocculation, electro-coagulation, UV-light degradation, and redox treatments, are being routinely used for abating dyes [1]. However, due to the ineffectiveness of these techniques in some way or the other, the present scenario requires better and improved wastewater-treatment measures. Recently, metal nanoparticles were reported as effective photocatalysts for degrading chemical complexes, under ambient temperature with visible light illumination [2]. This can be achieved by increasing the optical path of photons leading to a higher absorption rate of nanoparticles in the presence of a local electrical field [3]. These nanoparticles showed new and improved properties based on their morphological structures and characteristics as compared to bulk materials [4]. Moreover, scientists have also shown considerable interest in using nanoparticles for the photocatalytic degradation of dyes.

Biological synthesis of nanoparticles has been an interesting field of research due to its non-requirement of high pressure, energy, temperature, and toxic chemicals [5]. Particularly, silver (Ag) nanoparticles are outstanding with their unique optical, electrical, thermal, and electromagnetic properties [6–8]. Presently, microbes and plants are being exploited for large-scale synthesis of Ag nanoparticles. On the other hand, extracellular synthesis of nanoparticles by plants may be advantageous over chemical methods that meet the requirements of industrial applications [9]. Conversely, only a few reports are available on the use of marine plants for the synthesis of Ag nanoparticles [10–12]. Due to the complexity of marine environmental conditions, marine plants have become rich source of biologically active substances as compared to terrestrial plants [13]. Of all marine plants, seaweed mediated biosynthesis of Ag nanoparticles have been found to be efficient, cost effective, and environmental friendly [14]. Hence, the present study was aimed to study the photocatalytic degradation of methyl orange using Ag nanoparticles synthesized from marine seaweed, *Ulva lactuca*.

2. Materials and methods

2.1. Synthesis of Ag nanoparticles

Seaweed samples were collected from the Mandapam coast (9°16′47″N, 79°7′12″E), Gulf of Mannar, Tamil Nadu (southeast coast of India). The seaweed was morphologically identified as *U. lactuca* belonging to the family Chlorophyta. The seaweeds were

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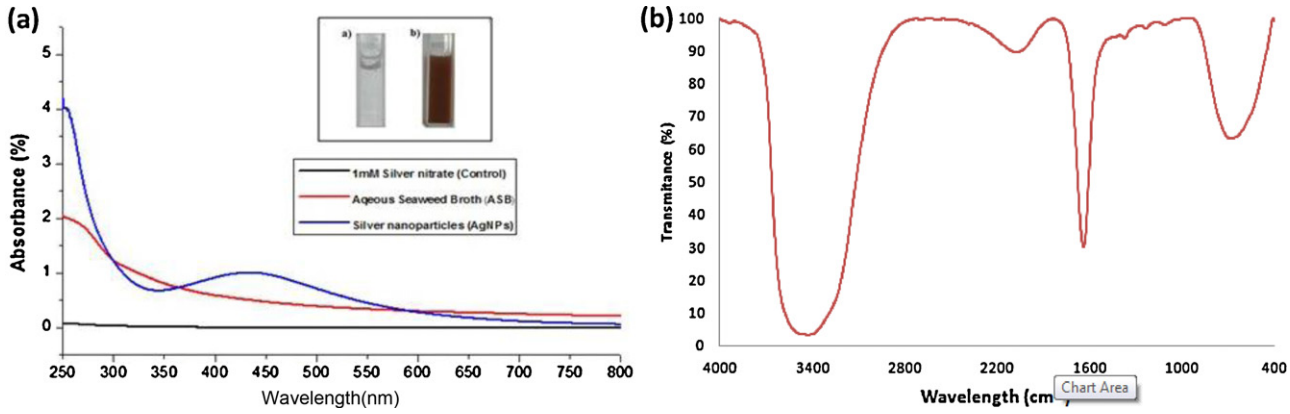

Fig. 1. (a) UV–visible spectrum [inset: color change: (a) control (1 mM silver nitrate) and (b) silver nanoparticles (AgNPs)] and (b) FT-IR spectrum.

cleaned with distilled water and shade dried for 15 days [15]. The dried materials were then powdered using a mixer grinder and refrigerated for further analysis. Later on, aqueous seaweed broth (ASB) was prepared by measuring 250 mg of powdered seaweed in a 250 ml Erlenmeyer flask containing 100 ml of sterile distilled water. The extract was boiled for 30 min and filtered through Whatmann No. 1 filter paper. To 50 ml of ASB, 50 ml of 1 mM silver nitrate ($AgNO_3$) solution was added [15]. The mixture was incubated at room temperature until further color change occurs. A control solution (1 mM $AgNO_3$ and ASB alone) was also kept under the same conditions.

2.2. Characterization of Ag nanoparticles

The synthesized Ag nanoparticles were well characterized by UV–visible spectrophotometer (Shimadzu, UV-2450, Japan) recorded at 200–800 nm. FT-IR spectral analysis was carried out in the range of 4000–400 cm^{-1} with a Spectrum RX-1 FT-IR spectrophotometer (Perkin–Elmer, USA) using KBr pellets. The morphology of the Ag nanoparticles was visualized using a field emission-scanning electron microscope (Carl Zeiss, SIGMA, UK). X-ray diffraction analysis (XRD) was performed by using Philps X'Pert Pro X-ray diffractometer by preparing thin film of powdered Ag nanoparticles. A zeta potential measurement of Ag nanoparticles was also carried out using Zetasizer Nano ZS90 (Malvern, UK).

2.3. Photocatalytic degradation

The photocatalytic degradation of methyl orange was evaluated by biosynthesized Ag nanoparticles [16]. All the experiments were performed outdoor with sun as the main source of light [17]. Prior to the experiment, a suspension was prepared by adding 20 mg of Ag nanoparticles to 50 ml of methyl orange solution (Fisher Scientific). Later, the mixture was allowed to stir constantly for about 30 min in darkness to ensure constant equilibrium of Ag nanoparticles in the organic solution. During the reaction, the mixture was kept under sunlight within a Pyrex glass beaker and stirred constantly. The mean temperature was found to be 29 °C with 10 h mean shine duration. The absorption spectrum of the suspension mixture was measured periodically using a UV–visible spectrophotometer (Shimadzu, UV-2450, Japan) after centrifugation to ensure the degradation of methyl orange solution.

3. Results and discussion

It is well know that seaweeds are extremely different from terrestrial plants with the ability to reduce silver ions [18]. However, when 1 mM $AgNO_3$ solution was added to the aqueous seaweed broth (ASB), no reaction occurred. Instead, after 48 h of incubation at room temperature, the color of the solution intensified to brown indicating the formation of Ag nanoparticles as shown in Fig. 1(a) inset. This is the first kind of report on biosynthesis of Ag nanoparticles using green seaweed *U. lactuca* (chlorophyta). The characteristic color change obtained may perhaps be due to the excitation of surface plasmon resonance (SPR) and reduction of $AgNO_3$ [19]. The control $AgNO_3$ solution remained as such without any change in color. This suggests that, the color intensity of the nanoparticles solution is directly proportional to the incubation time [20]. UV–visible spectroscopy is a convenient tool for measuring the reduction of metal ions based on optical properties called SPR. The reaction mixture has an absorption maximum of 430 nm suggesting the formation of Ag nanoparticles as shown in Fig. 1(a) [21]. Interestingly, there was no absorption peak in the control $AgNO_3$ solution or ASB [15]. The shape of the absorption band was found to be symmetrical, which indicates the presence of spherical-polydispersed nanoparticles and further confirmed by FE-SEM (~50 nm). Similar UV spectral signatures were obtained from Ag nanoparticles synthesized from seaweed extract of *Sargassum tennerrium* [11] and *Acanthophora spicifera* [14]. The incubation time plays an important role in the formation of nanoparticles by reducing the silver ions at room temperature. Our results showed that, there is no further changes in UV–visible spectrum signifying the reaction have come to an end. Thus, it is evident from this experiment; the formation of nanoparticles in solution is time dependent [22]. Intense FT-IR bands were observed at 3429 cm^{-1}, 1637 cm^{-1} and 685 cm^{-1}, which indicated the presence of molecular functional groups that are responsible for the reduction of silver ions as shown in Fig. 1(b). FT-IR peaks unveil the presence of phenolic compounds (3429 cm^{-1}) with hydroxyl group (O—H) bonded directly to an aromatic hydrocarbon group (685 cm^{-1}) [15]. The band at 1637 cm^{-1} is designated to the vibrational frequencies corresponding to amide I protein. Justifying the above statement, *U. lactuca* possess to have a protein concentration of 9–33% of its dry weight. The results entail that the phenolic compounds and protein may play a vital role in the formation of Ag nanoparticles [15]. However, several reports have suggested that the formation of Ag nanoparticles might be due to the presence of proteins, free amine, carbonyl and phenolic groups [22–24]. These functional groups may encapsulate the surface of silver ions by stabilizing the nanoparticles as capping agents. Though the exact mechanism involved in the formation of Ag nanoparticles is still a debated.

X-ray diffraction patterns of synthesized Ag nanoparticles were shown in Fig. 2(a). Almost eight different peaks were observed in the spectra at 2θ values of 27.89°, 32.31°, 38.14°, 46.29°, 54.87°, 57.53°, 67.47°, 74.45°, and 76.78°. These values were index to (1 1 0), (1 1 1), (2 0 0), (2 1 1), (2 2 0), (1 0 3), (1 2 3), and (0 0 4)

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