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Microwave-assisted green synthesis of silver nanoparticles and the study on catalytic activity in the degradation of dyes

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ABSTRACT

Biogenic methods are considered to be a safer alternative to usual physical and chemical methods of nanosynthesis due to their environment friendly nature and cost effectiveness. One major shortcoming of biological methods is their characteristically slow nature. In this study, we report a novel microwave-assisted green method for the rapid synthesis of silver nanoparticles. We synthesized silver nanoparticles by microwave irradiation using the leaf extract of *Biophytum sensitivum* as both the reducing and stabilizing agent. The nanoparticles are characterized by UV–vis, FTIR, XRD and HR-TEM studies. The FTIR spectrum provides sufficient evidences for the involvement of phytochemicals in stabilizing the nanoparticles. The XRD and HR-TEM studies clearly demonstrate the crystalline nature of the nanoparticles. From the TEM images, the silver nanoparticles are found to be almost spherical with an average diameter of 19.06 nm. The synthesized silver nanoparticles have been successfully applied as a catalyst in the degradation of methyl orange and methylene blue by $NaBH_4$.

1. Introduction

Dye effluents from paper, plastic, food, textile and pharmaceutical industries are now a major threat to the environment due to the substantial pollution problems caused by them. The release of these coloured materials into the water bodies causes eutrophication, reduces the reoxygenation capacity and makes severe damage to the aquatic organisms by hindering the infiltration of sunlight [1,2]. In addition, many of these dyes are mutagenic and carcinogenic and hence cause substantial injury to human life [3,4]. Therefore it is necessary to remove these dyes from our water resources. Conventional water treatment techniques include adsorption, ultrafiltration, biodegradation, chemical, photochemical and electrochemical methods [5–9]. Due to the chemical stability, the dye pollutants are usually resistant to devastation by physicochemical methods. Even though biodegradation methods are cost effective, they are inherently slow and are not effective for dye degradation as these are toxic to microorganisms [10,11]. In recent years, nanocatalysis has emerged as an alternative to conventional water treatment methods. The finite size, large surface area to volume ratio and size dependent reactivity have made metal nanoparticles an efficient catalyst [12]. Nowadays nanocatalysts are widely used for the effective removal of dye contaminants [13–16].

Among metal nanoparticles, silver nanoparticles (AgNPs) still seems to be fascinating due to their excellent optical and electronic properties as well as their wide applications in various fields such as catalysis, optics, biomedical, pharmaceutical and sensor technology. Several synthetic methodologies are now available for the synthesis of nanoscale silver such as chemical [17], photochemical [18], electrochemical [19], microemulsion [20], and microwave [21]. Most of these methods involve the use of toxic chemicals and severe reaction conditions which lead to chemical toxicity and environmental pollution. The negative impacts of chemical methods and the increasing focus on green chemistry have augmented the importance of biological method of nanosynthesis. The biomediated methods are considered to be a feasible alternative to physical and chemical methods because of its ease, eco-friendly nature and cost effectiveness. Several groups have reported the synthesis of silver nanoparticles using plant extracts as both the reducing and capping agent [22–25]. One drawback of biological methods is that they are slow compared to chemical methods. This limitation can be overcome by incorporating microwave chemistry with biomediated methods. Microwave-assisted biosynthesis using plant extracts as both reducing and stabilizing agent is a viable method for the rapid and easy synthesis of silver nanoparticles. Microwave irradiation causes rapid and uniform heating of the reaction medium and thus provides homogeneous nucleation and growth conditions resulting in monodispersed nanoparticles in short reaction time [26]. In our recent work, we have reported the microwave-assisted biosynthesis of silver nanoparticles using the leaf extract of *Aerva lanata* [27].

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In this article, we present a novel microwave-assisted method for the synthesis of silver nanoparticles using the aqueous leaf extract of the plant *Biophytum sensitivum* as both the reducing and capping agent. This is a simple, one pot, and green method for the quick and facile synthesis of silver nanoparticles. *B. sensitivum* is a small annual herb belonging to the family *Oxalidaceae*. The flowers of the plant are significant for its medicinal, cultural and traditional values. *B. sensitivum* has several medicinal properties and the plant parts are used in the treatment of asthma, inflammatory diseases and diabetes. The biological activity of the plant shows hypoglycemic, immunomodulatory, chemoprotective, hypocholesterolemic, antiinflammatory, antitumor, and antibacterial activity [28,29]. The phytochemical analysis of the plant showed the presence of amentoflavone, 3′,8″-biapigenin, proanthocyanidins and phenolic compounds [30]. The catalytic activity of the silver nanoparticles synthesized using *B. sensitivum* leaf extract (AgNP-biophytum) was investigated by using them in the degradation reactions of methyl orange and methylene blue by $NaBH_4$.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$), methyl orange, methylene blue and sodium borohydride ($NaBH_4$) of analytical grade were purchased from Merck (India) and used as such without further purification. All aqueous solutions were prepared using double distilled water.

2.2. Methods

2.2.1. Preparation of *B. sensitivum* leaf extract

Green fresh leaves of *B. sensitivum* were collected and authenticated. Twenty five grams of the leaves were washed thoroughly with distilled water to remove any dirt particles adhering to it and then it was chopped into small pieces. These were taken in a round bottom flask fitted with water condenser and boiled for 10 min with 100 mL of double distilled water. It was cooled and filtered through Whatman No. 1 filter paper. The extract thus obtained was stored at 4 °C for further use.

2.2.2. Biosynthesis of silver nanoparticles

In microwave-assisted synthesis, 90 mL of 1 mM silver nitrate solution was taken in a 250 mL beaker. To this, 10 mL *B. sensitivum* leaf extract was added and stirred well. This was placed in a domestic microwave oven (Sharp R-219T (W)) operating at a power of 800 W and frequency 2450 MHz and was subjected to microwave irradiation for 3 min. The formation of silver nanoparticles (AgNP-biophytum) was monitored using a UV–vis spectrometer by analysing the reaction mixture after 0, 1, 2 and 3 min of microwave irradiation in the range of 250–700 nm. The silver nanoparticle solution was then centrifuged at a speed of 10,000 rpm for 10 min. The supernatant was decanted and the nanoparticles were redispersed in distilled water. The above process was repeated thrice in order to remove impurities and any unused biomaterials. The purified sample was freeze dried to get dry particles. The nanosynthesis was also carried out at room temperature without microwave-assistance in order to learn the effect of microwave heating on the rate of formation of nanoparticles. For that, 10 mL of *B. sensitivum* extract was added to 90 mL of 1 mM aqueous solution of silver nitrate and the reaction mixture was kept at room temperature for 24 h. The reaction mixture was subjected to UV–vis spectroscopic analysis at regular intervals in order to examine the formation of AgNP-biophytum.

2.2.3. Catalytic degradation of methyl orange

The catalytic degradation of methyl orange by $NaBH_4$ was studied as follows. To 2 mL of aqueous methyl orange solution (0.01×10^{-2} M) Q3 was taken in a quartz cell of 1 cm path length and 0.5 mL freshly prepared $NaBH_4$ solution (0.06 M) was added. Followed by this, 0.5 mL of AgNP-biophytum solution of a definite concentration was added to start the reaction. The variation in the concentration of methyl orange with time was monitored using UV–vis spectrophotometry by following the change in the absorbance of the peak at 464 nm. The absorption spectra were recorded at 1 min intervals in the range of 200–600 nm at an ambient temperature.

2.2.4. Catalytic degradation of methylene blue

To study the catalytic degradation of methylene blue by $NaBH_4$, 0.5 mL of newly prepared $NaBH_4$ solution (0.06 M) was added to 2 mL of aqueous methylene blue solution (0.08×10^{-3} M) in a quartz cuvette. Then 0.5 mL nanocatalyst solution of a certain concentration was added and the progress of the reaction was followed spectrophotometrically by monitoring the change in the intensity of the peak at 664 nm. The absorption spectra were recorded at 1 min intervals in the range of 400–800 nm at an ambient temperature.

2.2.5. Characterization

UV–vis spectral analysis was carried out using a Shimadzu UV-2450 spectrophotometer. FTIR spectrum was recorded on a Perkin Elmer-400 spectrometer with ATR attachment. XRD measurement was made on a PANalytic X'PERT-PRO X-ray spectrometer. The XRD sample was prepared by drop coating the nanoparticle solution on a glass slide followed by drying under ambient condition. High resolution-transmission electron microscopic (HR-TEM) images were taken using a JEOL JEM-2100 microscope. Q4

3. Results and discussion

3.1. UV–vis spectroscopic studies

UV–vis spectroscopy is a valuable tool to establish the formation and stability of metal nanoparticles because nanoparticle solution shows

Fig. 1. Digital images of (a) *Biophytum sensitivum* plant, (b) mixture of plant extract and $AgNO_3$, and (c) AgNP-biophytum.

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