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An efficient photo catalytic activity of green synthesized silver nanoparticles using *Salvadora persica* stem extract

Kamran Tahir [a], Sadia Nazir [b], Baoshan Li [a,*], Arif Ullah Khan [a], Zia Ul Haq Khan [a], Aftab Ahmad [a], Faheem Ullah Khan [a]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] Institute of Chemical Sciences, Gomal University, D.I.Khan, KP, Pakistan

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ABSTRACT

A novel and ecofriendly procedure was developed for the synthesis of silver nanoparticles (AgNPs). The aqueous stem extract of *Salvadora persica* was used as reducing and capping agent. The formation of nanoparticles was observed at different temperatures and concentrations of the stem extract. Results indicated that at high temperature (120 °C) and concentration (30 mL), the reducing and stabilizing ability of the stem extract was declined. The synthesized AgNPs were highly dispersed, small sized (1–6 nm) and spherical in shape. The AgNPs were evaluated for photo degradation activity against methylene blue (MB) as an experimental substrate. Effect of various experimental conditions, such as catalyst amount, irradiation time and shape, size and dispersion of AgNPs were also investigated on the photo degradation of MB. The irradiation time experiment showed that photo degradation of MB was a rapid process and decomposed 96% in 80 min. The strong activities of AgNPs confirmed the significant application in water purification by converting hazardous materials into non-hazardous one.

1. Introduction

Nanoparticles of noble metals have rich applications in the fields of material science, medicine, biology, physics and chemistry [1]. Among these noble metals silver has attracted great attention of researchers due to its unique properties like good electrical conductivity, chemical stability, magnetic property, catalytic performance, phototonus, electrochemical and antimicrobial activities [2]. It has many applications in drug delivery [3], biomedicine [4], agriculture [5], food industry [6], water treatment [7], textile industries [8], biosensors [9,10], and as antibacterial activity [11]. Natural resources have the capability to reduce metal ions into metal nanoparticles [12,13]. The shape, size, morphology and dispersion of the nanoparticles play an important role in controlling the physical, chemical and biological properties. To synthesize highly disperse nanoparticles, chemical reduction method was frequently used in the presence of stabilizing agent. But the chemical syntheses of metal nanoparticles are expansive, poisonous to surrounding and energy expenditure. In recent years the green syntheses of nanoparticles have got enormous attention over the chemical and physical syntheses as it is a harmless, hygienic and ecofriendly route which includes benign reaction media and non-hazardous solvents. The biosynthesized nanoparticles are considered as an important branch of nanotechnology. The Biosyntheses of nanoparticles using fungi [14,15], bacteria [16], plants [17–23], algae [24], as well as phytochemical compounds [25,26] have been reported.

Salvadora persica is a plant of the genus *Salvadora* which are frequently found in Asia and South Africa [27]. *Salvadora* species have a number of medicinal applications and almost all parts of this plant (i.e. stem, leaves and roots) have been found to be pharmaceutically important [28–30]. This plant mostly used for the purpose of teeth cleaning. It is also known as Mustard Tree [31,32], Toothbrush Tree [33], Salt Brush Gudaphala, Pilu, Jhak, Chotapilu, Jhal and Piludi or Pilu. Because of the presence of fluoride in stem of *S. persica* it is used as oral hygiene tool or used as a usual toothbrush [34,35]. Stem shows anti-plaque effect more as compare to chlorhexidine gluconate [28]. Stem extracts show anti-caries [34], anti-microbial [36], anticonvulsant, antispasmodial [37] and sedative effects [38]. Bark of the stem of *S. persica* is used for gastric troubles and as an ascarifuge. The water soluble organic and inorganic hazardous compounds coming from industries have adverse effect on the living environment. Among all these industrial pollutants, synthetic dyes are considered to be the more toxic and common. Some dyes are carcinogenic and toxic to living world which

* Corresponding author.
E-mail addresses: bsli@mail.buct.edu.cn, zeolite.catalyst@gmail.com (B. Li).

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have adverse effect on humans and other organisms that come into contact with water containing these dyes [39,40].

Among all the organic dyes methylene blue (MB) is widely used in textile industries to colorize the products. MB is very toxic dye and can cause eye burns in humans and animals, dyspnea, skin irritation, tachycardia, cyanosis, convulsions, and if ingested can cause nausea, diarrhea, gastrointestinal tract irritation, vomiting, etc. MB is a stable organic dye and its photo degradation is a very difficult task. Photo degradation of organic dyes has been widely used in environmental protection and waste water treatments [41,42]. Various methods have been used for the removal of organic dyes from water such as chemical coagulation, flotation, ion exchange, membrane filtration, adsorption and oxidation [43,44]. Alternatively these methods have some major limitations such as higher dye concentration, inadequate dye removal, expansive and high energy conditions [45].

In research work, the photo degradation of MB was done by the green synthesized AgNPs. This is eco-friendly route using *S. persica* stem extract as the reducing and capping agent. This method is cheap and requires low energy conditions and overcomes the limitations of other methods. To the best of our knowledge this is the first report about the photo degradation of MB by green synthesized AgNPs using *S. persica* stem extract.

2. Materials and methods

2.1. Preparation of S. persica stem extract

S. persica stem was collected from local market in Pakistan and washed three times with distilled water. Amount of 200 g of *S. persica* stem was ground into fine powder and then mixed with de-ionized water, stirred at 60 °C for 3 h and filtered to get the extract.

2.2. Synthesis of silver nanoparticles using S. persica stem extract

For AgNPs synthesis, amount of 15 ml of S. persica stem extract was added to 70 ml of $3 \times 10{-}2$ M aqueous solution of silver nitrate in 150 ml beaker with continuous stirring. The formation of AgNPs was studied by the change in color from colorless to black within 70 min as shown in (Fig. 1). The appearance of black color is the clear indication of the formation of AgNPs. The black color appears due to surface Plasmon resonance in AgNPs. The AgNPs suspension thus obtained was separated from water with the help of repeated centrifugation at 10,000 rpm for 15 min. Then they were freeze dried by means of VirTis freeze mobile 6ES freeze drier.

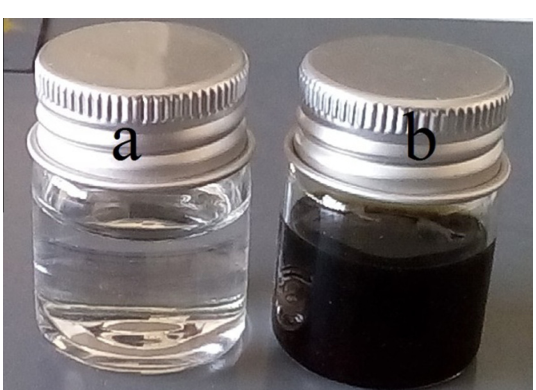

Fig. 1. Photographs of (a) silver nitrate in water and (b) AgNPs, water, stem extract after 60 min.

2.3. Photo catalytic activity

To test the photo catalytic activity of AgNPs, degradation of MB in aqueous solution was used. A UV light was used as light source. Amount of 8 mg of AgNPs was added into 70 mL of MB solution (15 mg/L). A control setup, having no AgNPs was also monitored. The suspension was magnetically stirred in dark for 30 min to make sure the equilibrium of the working solution prior to irradiation. After preparation of the suspension it was put under the UV light, and checked the degradation of MB solution after every 20 min.

3. Result and Discussion

3.1. Preparation

3.1.1. UV–vis Analysis

The UV–vis spectroscopy is used to examine the surface Plasmon resonance (SPR) peak of AgNPs. The formation of AgNPs was evaluated at different time interval inset in (Fig. 2a). The UV–vis spectra were recorded after every 5 min of time interval and AgNPs almost reduced in 50 min. The absorption peaks at around 418 nm stand for AgNPs which are due to the surface plasmon resonance excitation. It is well known that the surface plasmon resonance peak is dependent on the size and shape of the nanoparticles formed [46]. It was noted that the intensity of absorption peaks of AgNPs increases and broadness of the peaks decreases with increase in time. The formation mechanism of AgNPs can be represented by (Scheme. 1).

Vilchis-Nestor et al. synthesized stable AgNPs within 4 h reaction using Camellia sinensis extract [47]. Chandran et al. synthesized Ag nanoparticles within 24 h using Aloe vera [48].

In the present study the stable AgNPs were synthesized within 1 an hour. The formation of AgNPs was checked after every 5 min and the intensity of the absorption peaks increased with the passage of time; confirmed the reduction of Ag ions into Ag metals. The absorption recorded after 100 min showed the same intensity inset in (Fig. 2b) which revealed that this reaction was completed within one an hour. Thus it is clear that the *S. persica* stem extract have the strong ability to reduce and stabilize AgNPs.

3.1.2. Effect of temperature on the reaction rate

The surface plasmon resonance spectra of the AgNPs were taken after heating at different temperatures i.e. 25 °C, 50 °C and 120 °C as shown in (Fig. 2c). By increasing the temperature from 25 °C to 50 °C an increase in the sharpness of the peak was found which may be due to increase in the rate of reaction [49]. This sharpness of the peak is due to the small size of synthesized nanoparticles [50,51]. Alternatively an increase in the broadness of the peak occurred at 120 °C showing that the reducing and stabilizing ability of the stem extract was low at higher temperature. It may be occur due to decomposition of organic compounds because most of the organic compounds are stable at temperature lower than 100 °C.

3.1.3. Effect of leaf extract concentrations on the size of AgNPs

We mixed different concentrations of *S. persica* stem extract with 1 mM salt of silver to observe the effect of extract concentrations on biogenic synthesis of AgNPs. It is obvious from (Fig. 2d) that the surface plasmon resonance peak for AgNPs undergoes blue shift by decreasing the concentration of stem extract suggesting the possible decrease in size. The (Fig. 2e) also demonstrates that the wavelength of the absorption peak increases with increase in concentration of the extract. By increasing the concentration of the stem extract up to 30 ml, an increase in the broadness of