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Photocatalytic, antimicrobial activities of biogenic silver nanoparticles and electrochemical degradation of water soluble dyes at glassy carbon/silver modified past electrode using buffer solution

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ABSTRACT

In the present research work a novel, nontoxic and ecofriendly procedure was developed for the green synthesis of silver nano particle (AgNPs) using *Caruluma edulis* (*C. edulis*) extract act as reductant as well as stabilizer agents. The formation of AgNPs was confirmed by UV/Vis spectroscopy. The small and spherical sizes of AgNPs were conformed from high resolution transmission electron microscopy (HRTEM) analysis and were found in the range of 2–10 nm, which were highly dispersion without any aggregation. The crystalline structure of AgNPs was conformed from X-ray diffraction (XRD) analysis. For the elemental composition EDX was used and FTIR helped to determine the type of organic compounds in the extract. The potential electrochemical property of modified silver electrode was also studied. The AgNPs showed prominent antibacterial motion with MIC values of 125 μg/mL against *Bacillus subtilis* and *Staphylococcus aureus* while 250 μg/mL against *Escherichia coli*. High cell constituents' release was exhibited by *B. subtilis* with 2 × MIC value of silver nanoparticles. Silver nanoparticles also showed significant DPPH free radical scavenging activity. This research would have an important implication for the synthesis of more efficient antimicrobial and antioxidant agent. The AgNP modified electrode (GC/AgNPs) exhibited an excellent electro-catalytic activity toward the redox reaction of phenolic compounds. The AgNPs were evaluated for electrochemical degradation of bromothymol blue (BTB) dyes which showed a significant activity. From the strong reductive properties it is obvious that AgNPs can be used in water sanitization and converting some organic perilous in to non-hazardous materials. The AgNPs showed potential applications in the field of electro chemistry, sensor, catalyst, nano-devices and medical.

1. Introduction

Green nanotechnology is an area of interest having significant focus in the present scenario with important objective of facilitating the manufacture of nanotechnology-based products eco-friendly and safer for all beings with sustainable commercial viability. Nanoparticles of noble metals have rich applications in the fields of material science, medicine, biology, physics and chemistry [1–6]. Silver metals are attractive among the noble metals due to its exclusive properties like electrochemical, electrical conductivity, photo catalytic, chemical stability, magnetic, chemo catalytic and antimicrobial activities [7–12]. Silver plays an important role in drug delivery [13], water treatment [14], food industry [15], biosensor [16,17], agriculture [18] and textile industries [19]. Different methods are used to reduce Ag^{+} for example, use of γ-rays [20], irradiation [21], UV heating and electrochemical reduction [22], application of reducing chemicals, such as hydrazine [23], sodium borohydride [24–26], polyethylene glycerol [27], *N,N*-dimethyl formamide [28], glucose [29], ethylene glycol [30], formaldehyde [231], and sodium in liquid ammonia [32]. However, there is still a need for a more economic, commercially viable as well environmentally green synthesis route to synthesize AgNPs. The green synthesis of AgNPs involves three main steps, which must be evaluated based on green chemistry perspectives, including selection of solvent medium, reducing agent and nontoxic stabilizers for AgNPs [33]. Due to the improvement of antibiotic resistance in pathogenic bacteria, the pharmaceutical companies and researchers are searching for novel antimicrobials and

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the AgNPs are capable candidate for the same. The reduction of Ag^{+} ions leads to the formation of silver atoms (Ag) which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of colloidal AgNPs. When the colloidal particles are much smaller than the wavelength of visible light, the solution possesses characteristic yellow color with an intense band in the 380–430 nm range and other less intense bands at longer wavelength in the UV–visible absorption spectrum. In the present work we studied the antioxidant (DPPH free radical scavenging), antibacterial activities against Gram positive and Gram negative bacteria strains. Further we studied the potential photocatalytic and chemo catalytic properties of these AgNPs. Here we reported first time electrochemical degradation of dyes bromothymol blue (BTB) at Ag/GC modified past electrode.

2. Materials and Methods

2.1. Preparation of Caruluma edulis Extract

Caruluma edulis was collected from Bannu in Pakistan and washed several times with distilled water and dried under shade for several days and then grinded it into fine powders. Then 40 g of it was mixed with 100 mL of deionized water and stirred at 60 °C for 3 h and further filtered to get aqueous extract.

2.2. Synthesis of Silver Nanoparticles Using Caruluma edulis Extract

For silver nanoparticle synthesis, an amount of 20 mL of *C. edulis* extract was added to 90 mL of 3×10^{-2} M aqueous solution of silver nitrate in 150 mL beaker with continuous stirring at room temperature. AgNPs were separated from the colloidal solution by repeated centrifugation at 12,000 rpm for 10 min at 4 °C. Then the Ag nanoparticles were freeze dried using Vir Tis freeze mobile 6ES freeze drier.

2.3. Microorganisms

Three food-borne pathogens including *Escherichia coli ATCC 8739*, *Staphylococcus aureus ATCC 6538* and *Bacillus subtilis ATCC 6633* were used in antimicrobial assay. These strains were maintained on agar slants at 4 °C in the College of Life Science and Technology, Beijing University of Chemical Technology, Beijing for antimicrobial tests. Microbes were incubated overnight at 37 °C in the Mueller-Hinton broth (Oxoid) at pH 7.4. Cephalexin (50 μL of 4 mg/mL) in sterile DD water was used as standard drug.

2.4. Antimicrobial Screening

2.4.1. Screening for Antibacterial Activity

The antibacterial commotion was resolute through agar well diffusion method [34]. The bacterial strains were grown-up in nutrient broth at 37 °C for 24 h incubation till turbidity became equivalent to Mc-Farland 0.5 turbidity normal. The inocula of the *B. subtilis*, *S. aureus* and *E. coli* were streaked on to the condensed Muller Hinton agar (Oxoid) in petri plates by a sterilized cotton swab in order to make sure a uniform thick lawn or layer of growth following incubation. Wells of 8 mm in diameter were formed with the help of sterilized cork borer on to nutrient agar plates. The AgNPs (50 μL of 4 mg/mL) in sterile DD water were put into the wells and the plates were allowed to stay for 2 h at room temperature. Finally, the plates were incubated at 37 °C for 20–24 h and the resulting diameters of zones of inhibition were measured. The experiments were repeated three times and the data were calculated as means ± SD.

2.4.2. Determination of Minimum Inhibitory Concentration (MIC)

Minimum inhibitory concentration (MIC) of AgNPs was determined by agar dilution method [35]. The sterilized Muller Hinton Agar (oxoid) was cooled to 50 °C and 19 mL of this was added to sterilized test tubes which contained 1 mL of different concentrations of AgNPs. This mixture was smoothly shaken, mixed and poured into pre-labeled sterile Petri dishes. Petri dishes having only growth media were prepared in the same way so as to serve for comparison with Petri plates containing AgNPs. The concentrations of the AgNPs used in this test were ranged from 15.62 to 2000 μg/mL. The suspensions of the respective microorganisms having density adjusted to 0.5 Mc-Farland turbidity standards were inoculated onto the series of agar plates using standard loop. The plates were then incubated at 37 °C for 24 h. The lowest concentration which inhibited the growth of the respective microorganisms was taken as MIC. All tests were carried out in triplicate.

2.4.3. DPPH Free Radical Scavenging Assay

DPPH radical scavenging assay for AgNPs was performed as previously described [36] with a little modification. 0.5 mL of 1 mM DPPH was separately mixed with different concentrations (0.031–1 mg/mL) of AgNPs and incubated in dark for 30 min. After incubation the absorbance of the samples was determined by UV 1100 spectrophotometer (MAPADA instruments) at 517 nm against methanol as a blank. Vitamin C was used as standard and DPPH methanol reagent without sample was used as control. The percentage of inhibition was calculated by the following formula.

$$\%\ \text{of inhibition} = [(\text{Absorbance}_{\text{control}} - \text{Absorbance}_{\text{test}}) / \text{Absorbance}_{\text{control}}] \times 100.$$

2.4.4. Statistical Analysis

All experiments were performed in triplicate. The data was recorded as mean ± standard deviation (SD) for the measurements. The data was statistically analyzed by the statistical package (Graph Pad prism V5).

2.5. Photo Catalytic Activity

To test the photo catalytic activity of AgNPs, degradation of bromothymol blue dye in aqueous solution was used. A UV light was used as light source. An amount of 12 mg of AgNPs was added into 70 mL of bromothymol blue 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 the degradation of bromothymol blue solution was checked after every 35 min.

2.6. Assembling of AgNP Modified Glassy Carbon Electrode

The bare glassy carbon electrode (GCE) was polished into a mirror-like surface with 0.5 and 0.05 mm alpha Al_2O_3 and then rinsed ultrasonically with water bath, so that any physically adsorbed species is removed. The cleaned GC electrode was modified by dip coating with AgNPs, using immersion times (2 h) in the colloidal nanoparticle solutions.

3. Results & Discussion

3.1. UV/Visible Spectroscopy 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. 1A. The UV–vis spectra were recorded after every 10 min of time interval and AgNPs almost reduced in 60 min. The absorption peaks at around 410 nm stand for AgNPs which are due to the SPR excitation. It is well known that the SPR peak is dependent on the size and shape of the nanoparticles formed [37]. The spherical shape nanoparticles show single plasmonic band, while isotropic nanoparticles show two or more bands due to quadrupole and multipole plasmon excitations [38]. H. Bar et al. synthesized