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Electrochemical preparation of AgNPs within pullulan matrix as an electrolyte

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Abstract: In this article, pullulan (pl) has been used as electrolyte for silver nanoparticles formation (AgNPs) using electrochemical process. The formation and stability of AgNPs, the reducing and the stabilizing ability of pullulan was examined using UV– Visible spectroscopy, Transmission electron microscope (TEM) analysis, inductively coupled plasma optical emission spectroscopy (ICP-OES), Zeta potential analysis and stability test .

The results revealed that silver ions steadily electro-released within pullulan electrolyte and reduced to silver nanoparticles due to pullulan functional groups. UV-Vis patterns introduced that an emerging peak centered at around 400 nm with descending behavior in intensity as a function of the electro-release time. ICP measurement presented that the concentration of AgNPs was 742 mgL^{-1}. TEM images and the size distribution curves explored that spherical AgNPs formed with average diameter 11 nm. In addition, the zeta potential value of the prepared solution was +2.5 ± 4.26 mV.

keywords: Electrochemical synthesis – pullulan- Silver Nanoparticles

1.Introduction

Currently, Metallic nanoparticles (MNPs) have a broad variety of applications in the nutrition, biomedical, and electronic sectors. Of these, zinc, copper, gold and silver induced metal nanoparticles getting much interest due to their widespread usage. Although several physical and chemical techniques have been used to prepare metallic nanoparticles, utilizing ecologically friendly and non-harmful biological substances such as microbes, plant extracts, and actinomycetes has been integrated into the production of MNPs [1-6].

Ag NPs have been produced by using Several techniques. Microemulsion [7,8], photoreduction [9], chemical reduction [10,11], γ-radiation[12], laser ablation[13], supercritical liquid[14], and magnetron sputtering[15] are some of these techniques. Some of these techniques demonstrated outstanding management of particle shape and size, and the resulting AgNPs demonstrated better properties. However, the majority of synthesis technologies rely on organic solvents, which in turn pose significant risks [16,17] and poisonous reducing agents [18]. Furthermore, the chemicals used are hazardous and represent potential biological and environmental risks [19]. Even the physical techniques used to prepare Ag NPs necessitate reasonably expensive tools and particular conditions.

The electrochemical method was used by Reetz and Helbig [20] for the first time to synthesize nanoparticles (NPs). To do this, a metal sheet was used as a anode, which dissolved in the intermediate forming metal ions, which were reduced at the cathode forming metallic particles in acetonitrile containing quaternary ammonium salts[21]. Using the same strategy, potentiostatic or galvanostatic polarization of Ag in an alcoholic medium used to prepare silver nanoparticles [22]. Additionally, poly (N-vinyl pyrrolidone) (PVP) has been utilized to stabilize Ag particles by using electrochemical method [23].

In recent years, an innovative concept called 'green' synthesizing silver nanoparticles via polysaccharides from fungi were used as renewable polymeric materials to stabilize synthetic NPs[24]. The biopolymers that are most frequently used to make AgNPs are gelatin [25, 26], dextran [1, 27], chitosan [28, 29], albumin [30], sodium alginate [31] and others. Pullulan, a fungus exopolysaccharide, has lately been used as a stabilizing and reducing agent by a small number of researchers [25, 32-35].

Pullulan is an unbranched, linear polymer composed of repetitive maltotriose units connected by α-(1 → 6) glycosidic bonds [36]. Pullulan structure is frequently viewed as a transitional structure between amylose and dextran [37]. Pullulan is a chemical compound with the molecular formula $(C_6H_{10}O_5)_n$ and a molecular weight range 4.5×10^4 to 6×10^5 Da and the cultivation factors have a significant impact on these properties[38]. It is a white in color, non-hygroscopic powder that dissolves easily and completely in cold and hot water, as well as in dilute alkalis. With the exception of formamide and dimethyl sulfoxide, it is insoluble in alcohol and other organic liquids [39]. Pullulan has hydrodynamic properties due to its chain flexibility in a solvent [40]. Pullulan begins to degrade at temperatures higher than its melting point of 250 °C. It is edible, colorless, odorless, non-mutagenic and non-toxic. Pullulan exhibits normal physiological activity due to the fact that its main chain contains a large concentration of hydroxyl groups.

This research looked into the green synthesis of solution pl-AgNPs through electrochemical oxidation. UV-Vis spectroscopy and electron microscopy images of the sample were studied, and the silver concentration was also determined using Inductively Coupled Plasma Spectroscopy (ICP) (ICP-OES). The stability and charge of the formed silver nanoparticles were studied by zeta potential.

2. Materials and methods

Materials

Pullulan was purchased from Alfa Aesar Karlsruhe (Germany). Anhydrous citric acid was bought from El Naser Pharmacitical Chemical (Egypt). Platinum (Pt) and Sliver (Ag) rectangular sheet (> 99.9%, Sigma Aldrich, St. Louis, MO, USA) and deionized water (DW) (resistivity > 2×10^8 Ω cm). All reagents were of analytical grade and used as received.

Methods

Preparation of pl-AgNPs

The pl-AgNPs were prepared through the electrochemical method. The sample was prepared inside an electrochemical cell, which is called the voltage method, using a constant voltage of 1.5 volts at a suitable resistance (BK, PRECISION 9201, Multi-Range Programmable DC Power Supply). The used cell consists of silver plate (anode) and platinum plate (cathode) separated by 1 cm. In this electrolyte solution, both electrodes are immersed vertically.

The electrolytic solution was made at room temperature by dissolving pl (1 wt%) in deionized water (DW) and stirring until total dissolution.7% (v/v) aqueous citric acid (1 M) was included in the previous solution. The electrochemical process took place for interval (2 h).

Characterizations

UV-vis spectra measurement

Using a dual-beam spectrophotometer (T80 double beam UV-vis spectrophotometer, pg instruments, UK), measurements in the UV-visible range were taken with a wavelength precision of 0.3 nm and falling between 190 and 1100 nm. For measurement, the samples to be measured were placed in a cuvette of 1 cm made of quartz at room temperature. To see any change in the solution as a result of the formation of AgNPs, 4 ml of the electrolyte solution formed was taken inside a cuvette of quartz and studied its surface plasmon resonance peak to verify the presence of silver in the electrolyte solution formed and also for indications of possible changes in the characteristic bands of pullulan during the synthesis process.

Transmission electron microscope (TEM) analysis

By studying TEM images (JEOL TEM-2100) that were captured with a CCD camera connected to it, the size and shape of the formed silver nanoparticles were determined. An ultrasonic cleaner (sonicator (XH-E412)) was used to sonicate the samples before being examined. To perform TEM measurements, a few drops of the synthesized solution containing silver were poured onto the copper grid that was coated with carbon, the solvent was allowed to evaporate very slowly at room temperature.

Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively coupled plasma spectrometry (ICP–MS, Agilent 7700X, 6 Australia) was used to precisely measure the concentration of silver in pl-AgNPs solution.

Zeta potential analysis

Surface charges were determined by Zeta size Nano-zs90 (Malvern Instruments, Malvern, UK), using deionized water the solution was diluted. The surface charge distribution was determined by three independent times at room temperature.

3. Results and Discussion

UV–visible spectroscopy analysis

Silver nanoparticles appear to have a large response to UV-visible absorption spectra due to surface plasmon resonance (SPR), so intense absorption peaks appear [41, 42]. Figure 1 depicts the UV-vis spectrum bands of silver nanoparticles obtained at different electro-release times of the silver ions (15, 30, 45, 60, 75, 90, 105 and 120) min within pullulan matrix. All spectra exhibit the formation of a localized absorbance spectrum in the region 380-430 nm, centered at 400 nm, attached to the standard plasmon resonance range of silver nanoparticles, which matches the distinctive SPR of conducting electrons from silver nanoparticle surfaces [41-43]. On the other hand, Figure 1 and 2 revealed that the intensity of the absorption band of AgNPs decreases as a function of the electro-release time of the silver ions. This may be assigned to pullulan ability to control the growth of the silver nanoparticle was weak a little bit, so freshly formed Ag atoms preferred the growth over than nucleation

Transmission electron microscopy (TEM)

Figure 3 displays the typical transmission electron microscopy (TEM) images and the associated particle size distribution of the AgNPs solution. As Figure 3 demonstrates, the obtained AgNPs were in bimodal size distribution of semi-spherical shapes. In depth, the results of the TEM images showed that the small particles had an average size of 11 nanometers, while the large particles had a size of 1 micrometer. this result is constituent with UV-Vis result, this may be assigned to the inability of the pullulan functional groups to surround the silver particles.

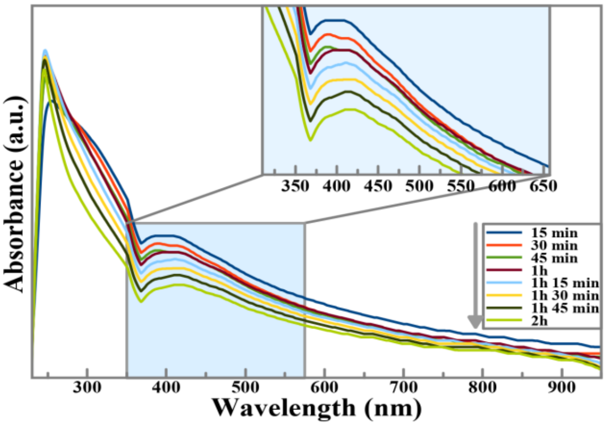

Figure 1: UV-Vis patterns of the prepared solution as a function of the electro-release time of the silver ions

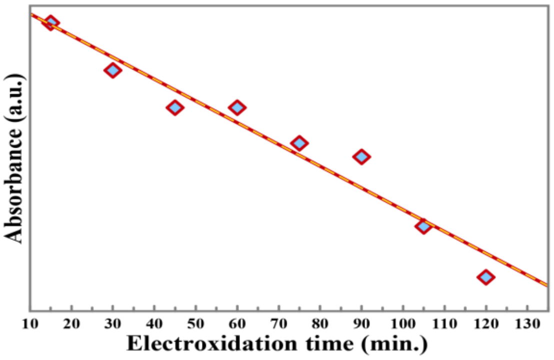

Figure 2: variation of the 400 nm peak intensity against the electro-release time of the silver ions

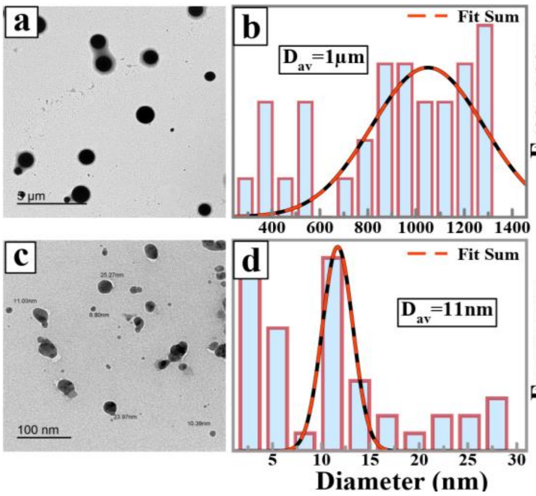

Figure 3: TEM images and the size distribution curves of the formed AgNP$_s$

ICP

(ICP) is a technique used to measure the concentration of AgNPs in the synthesized solution. The results showed that the silver concentration in the pl-AgNPs solution was **742** mgL^{-1}, which is regarded as an adequate quantity of electro-released silver throughout the matrix of polymeric material.

Zeta potential

Zeta potential of the synthesized solution, pl-AgNPs, was measured to show the stability of the AgNPs in the sample and it was found to be equal to +2.5 ± 4.26 mV as explored in Figure 4, proving instability of the NPs in the colloidal solution [44]. Pullulan exhibits an "uncharged state" in the form of a colloidal solution when utilized as a capping agent [35, 44].

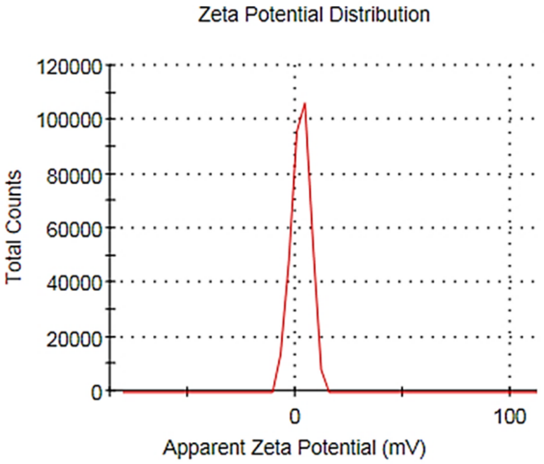

Figure 4: zeta potential distribution of the prepared pl-AgNPs solution.

4. Conclusion

Silver nanoparticles were prepared electrochemically in an aqueous solution of pullulan at room temperature. This method of preparation is easy, simple, environmentally friendly and takes place in one step. Pullulan is an efficient reducing agent but a poor stabilizing agent in silver nanoparticle production. The biopolymer structure used to cap silver ions affects the effectiveness of the produced nanoparticles. Freshly prepared pl-AgNPs showed that zeta potential +2.5 ± 4.26 mV, a very low value the result shows that the pullulan has a bad capping AgNPs. TEM images confirmed the silver nanoparticles synthesis with a bimodal size, 11 nm and 1 µm. The large size formed is attributed to the agglomeration of the particles due to the capping inability of pullulan.

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