Ultrasound Intensified Green Synthesis of Silver Nano particles using Camellia Sinensis Extract fortified with Lemon and Honey

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Abstract: Ultrasonic waves appear as an interesting way to improve process productivity. The present study reports a facile ultrasound intensified green synthesis of silver nano particles from the extract of Camellia Sinensis fortified with lemon and honey. The extract is acting both as reducing agent as well as capping agent. The synthesized silver nano particles have been characterized by UV-Vis spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis. The active organic groups responsible for the reduction of Ag\(^{+}\) ions to elemental silver were identified by Fourier Transform Infrared spectroscopy (FT-IR). The effect of ultrasound on the reduction reaction rate was found and was found to get enhanced with ultrasonic irradiation. Polydispersity of synthesized silver nano particles is minimized and also controlled by ultrasonication method. This novel method is rapid, facile and combines the advantage of both sonochemistry and green chemistry.

Key Words: Green synthesis; process intensification; ultrasound assisted synthesis; Bio-reduction.

Introduction

Metal nano particles exhibit distinct physical and chemical properties compared to their bulk counter parts due to the small size, shapes and controlled disparity. \(^{(1)}\) Silver nano particles have always attracted researchers due to its widespread application in various fields such as catalysis, sensors, \(^{(2)}\) electronics, biotechnology and in biomedicine as antibacterial, \(^{(3)}\) antiseptic, antimicrobial, \(^{(4)}\) antiviral agents etc. Though various conventional methods like electro-chemical, \(^{(5)}\) sol-gel process, \(^{(6)}\) chemical reduction, \(^{(7)}\) hydrothermal, \(^{(8)}\) Sonochemical \(^{(9)}\) microwave irradiation \(^{(10)}\) etc. methods are available for the synthesis of silver nano particles, in the past few decades there has been an extensive increase in the research for green synthesis \(^{(11-20)}\) of silver nano particles due to environmental concerns and sustainable development which makes it an attractive alternative to the conventional methods of synthesis. Green synthesis of silver nano articles using natural sources is currently under exploitation \(^{(21)}\).
Several polyphenolic catechins viz, (-) epicatechin (EC), (-) epicatechin-3-gallate (ECG), (-) epigallocatechin (EGC), (-) epigallocatechin-3-gallate (EGCG), (+) Catechin, and (+) gallocatechin (GC) which are present in the camelliasinensis extract are strong antioxidants and can potentially reduce silver salts. The reducing nature of camellia sinensis was enriched with lemon (citric acid component) and honey (poly saccharide). The process is further intensified by irradiation with ultrasonic waves. When the reactants are irradiated with ultrasound the alternating expansive and compressive acoustic waves create bubbles called cavities and it make the bubbles to oscillate. The oscillating bubbles accumulate the ultrasonic energy effectively and grows, when it becomes optimum in size, it collapses releasing the concentrated energy stored in the bubble within very short-time. The cavitation implosion is very localized and transient with a temperature of the order of thousands kelvin, that assists in the production of silver nano particles of smaller size and with reasonably faster rate.

Materials

Precursor- Silver Nitrate-purchased from Qualigens, India. Long leaves of camellia sinensis, natural honey and lemon.

Instrument: Wensor Digital Ultrasonic bath

Extract preparation:

One gram of well dried and powdered Camellia Sinesis was put into 50ml of water and boiled for about 15 minutes. The extract was filtered with Whatman No.1 filter paper. To the extract 5ml of Honey and 5ml of lemon juice was added. This aqueous extract was used to synthesize silver nano particles.

Results and Discussion

When 5ml of camelliasinensis with lemon and honey extract was added to 100ml of 0.001M Silver nitrate solution, Color of the solution changed gradually from pale yellow to reddish brown colour in fifteen minutes. Appearance of Reddish brown colour indicated the formation of silver nano particles. When the same amount of the precursor and the aqueous extract was irradiated with ultrasonic waves, it has taken only five minutes of time for the appearance of reddish brown color and thereby for the formation of silver nano particles. This may be due to the fact that in addition to the active groups (present in the extract) responsible for the bio-reduction, ultrasonic irradiation of aqueous liquids generate free radicals like H and OH. These free radicals also reduce Ag+ ions to Ag(0). Hence the reduction reaction rate got enhanced with sonication.

Characterization

UV-Visible Spectral Analysis:

The initial characterization of the synthesized silver particles was done by UV-Vis spectroscopy.

Sample: The bio- reduced aqueous component (0.5ml) was diluted ten times with double distilled water to avoid errors due to high optical density of the solution.

Instrument: Shimadzu UV 1650pc Spectrophotometer.
Metal nano particles have free electrons, which gives surface plasmon resonance absorption band due to the combined vibration of electrons of metal nano particles in resonance with light wave. The appearance of a sharp absorption peak at 425nm, is characteristic wavelength of silver and thereby confirms the formation of silver nano particles.

**Fourier Transform Infrared Spectral Analysis (FT-IR)**

**Sample:** The bio- reduced solution was centrifuged at 10,000 rpm for half an hour. The sample was grinded with KBr pellets, dried in infrared light and then subjected to FT-IR measurement.

**Instrument:** Shimadzu FT-IR Spectrophotometer.

**Spectrum Range:** Spectrum was recorded in the range of 4000-400 cm$^{-1}$.

The intense peak at 3442 cm$^{-1}$ correspond to N-H, O-H stretching vibrations of alkanes, amide, alcohol and H-bonded to phenols. Peaks at 2950, 2926 and at 2811 indicates the presence of very strong C-H stretching vibrations. The peak at 2080 corresponds to C=N stretching vibration. The peak at 1640 indicate C=C, C=O stretching vibrations of alkenes and amides. The peak at 1031 indicates C-O, C-N stretching vibrations and it
corresponds to the presence of alcohols, carboxylic acids, ethers, esters and aliphatic amines in the extract. The peak at 596, 532, and 452 corresponds to C-Cl, C-Br and C-F stretching vibrations of alkyl halides. So it can be assumed that the water soluble alkaloids, flavonoids and phenols present in the extract are acting as both capping agent as well as stabilizing agent.

**Energy Dispersive X-Ray Analysis (EDX)**

It is an analytical technique to identify the elemental composition of the specimen.

**Instrument:** The dried silver nanoparticles prepared were mounted on specimen stubs, and are examined under a Philips XL-30.

EDX attachment on the SEM provided the chemical analysis of the field as well as spot analyses of minute particles and confirmed the presence of specific elements. The presence of elemental silver in the reaction mixture was confirmed by EDX analysis. The silver nano particle exhibited an optical absorption band peak at 3 KeV which is typical of the absorption metallic silver nano particles.

**SEM Analysis**

**Sample:** Thin film of the sample was prepared on a carbon coated grid by just dropping a very small amount of the sample on the grid, extra solution was removed using a blotting paper and then the film on the SEM grid was allowed to dry by putting it under mercury lamp for 5 minutes.
SEM images of silver nano particles at different magnifications before and after ultrasonication reveal that the particles are predominantly spherical in shape. The average size ranges from 30.2 to 75.4 before ultrasonication. After ultrasonication, poly dispersed particle size of silver nano particles is reduced to an average size of 34.5 nm and almost of uniform particle size.

Conclusion
In this work, we were able to prepare silver nano particles by a clean, safe and rapid method using all natural sources, camellia sinensis, honey and lemon extract, and the process was intensified by ultrasonication. The synthesized silver nano particles have high potential applications in the biomedical field and this procedure has several advantages such as cost effectiveness, compatibility for medical and pharmaceutical applications as well as large scale production.

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