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Biogenic silver nanoparticles from *Trachyspermum ammi* (*Ajwain*) seeds extract for catalytic reduction of *p*-nitrophenol to *p*-aminophenol in excess of $NaBH_4$

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ABSTRACT

Plasmonic silver nanoparticles (AgNPs, size = 3–50 nm) were synthesized by biogenic reduction of aqueous $AgNO_3$ using *Trachyspermum ammi* (TA, *Ajwain*) seeds extract. Increase in concentration of TA, accelerated the reduction rate of Ag^+ and affected the AgNPs particle size. Pronounce effect of the AgNP's aging (24, 48 and 72 h) on particle concentration/size and their corresponding catalytic activity, was exhibited by the systems. Surface plasmonic resonance band centered between 420 and 430 nm wavelength, recognized as first exitonic peak of UV–vis absorption spectra of Ag NPs, was used to estimate the particle size (10–30 nm) of Ag NPs, which was consistent with the particle size observed with the FESEM (5–20 nm) and XRD observations (12.74 nm). XRD analysis also indicated that the silver nanoparticles were crystallized in the cubic crystal pattern. However, some cubic/rod like patterns grown along the 111 plane, was also observed by FESEM and HRTEM. ATR (Attenuated total reflectance) profile of aging of TA supported Ag NPs, exhibited the decrease in intensity of 3394, 1716 and 1618 cm^{-1} peaks with respect to the pristine TA extract sample. That reflects the increase in particle concentration with time (24–48 h). These peaks correspond to the O—H group, carbonyl group and C ═C stretching along with C—O—C and C—N stretching in TA-AgNPs aggregates. ATR and IR results suggested the presence of the reducing agent/phytochemicals (nicotinic acid, thymol, sugars, proteins, saponin, etc) incorporated NPs. Impedance study revealed that the rate of charge transfer in TA-Ag NPs aggregates is inversely proportional to the concentration of TA that confirms the stability of the Ag NPs in water. These biogenic Ag NPs are also characterized using transmission electron microscopy (TEM) and their corresponding energy dispersive X-ray analysis (EDX), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) studies, etc. On the basis of the above observations and optoelectronic characteristics, the most probable mechanism of biogenesis of the stable Ag NPs, is suggested. As-synthesized 24, 48 and 72 h aged Ag NPs, were tested for their catalytic reduction activity towards the conversion of *p*-nitro phenol to *p*-aminophenol in excess of $NaBH_4$. 48 h-aged Ag NPs show highest catalytic activity for conversion of *p*-nitrophenol to *p*-aminophenol in excess of $NaBH_4$ in terms of rate ($r = 0.34539\ min^{-1}$) with complete reduction time 12 min.

1. Introduction

Recently, metal nanoparticles have attracted immense attention of researchers over their bulk counterparts due to their versatile applicability in different areas [1–4]. These are magnetic, electronic, electrochemical, antimicrobial, corrosion, inhibition and optical performances. Because of their unmatched superb qualities, they can affect human life in various avatars such as biosensors, nano-molecular optoelectronic devices, bio-mimetic materials, catalysts in biomedicine, industrial and environmental fields. There are two most well-liked approaches for fabrication of nanoparticles. First is bottom to top or small to big approach, where the NPs gain the final shape by addition of small building blocks and prepared using supercritical liquid medium, templates, spinning, plasma or fire sparing, pyrolysis, sol-gel process, biological method, chemical vapour deposition, atomic condensation, etc. The second approach is top to bottom approach, which involves mechanical milling, electrochemical explosion, laser ablation, chemical etching, etc. Where, bigger particle cut down into small particles of different shapes. Morphology (shape and size) of the nanoparticles' is very important for deciding their optical, electronic, magnetic, and catalytic properties. These novel properties can be engineered by controlling the dimensions of metal nanoparticles. Beside

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the conventional practices of synthesizing metallic nanoparticles i.e. physical and chemical methods, the biogenic production is a better option due to its ease of fabrication via green route with non-toxic and non-poisonous ingredients, biocompatibility, mild reaction conditions, low cost, simplicity and eco-friendly nature of reaction, are the benefits of the biogenic synthesis. Therefore, this can be used as an economic and valuable alternative for the large scale production of metal nanoparticles. Biological materials/tools adopted in this method are fungi [5–7], bacteria [8–10], Bengal gram bean [11], yeasts [12], *Capsicum annuum* [13], quercetin [14], biomass of oat (*Avena sativa*) and wheat (*Triticum aestivum*) [15], honey [16], plants' extract, etc.

A wide range of metal NPs such as Au [17–21], Ag [22–23], TiO_2 [24], In_2O_3 [25], ZnO [26], CuO [27], etc, have been synthesized using herbal/plant extracts. Several plants have been explored for the synthesis of metal NPs including medicinal plants [26]. Use of plant extract and microbial cells in the synthesis of metal NPs, was triggered by existence of the several organic group/compounds such as carbonyl groups, terpenoids, phenolics, flavonones, amines, amides, proteins, pigments alkaloids and other reducing agents of the plant extract. In this research work, an aqueous seed extract of *Trachyspermum ammi* (TA; *Ajwain*) has been used to grow the metal (silver) nanoparticles. This plant is the native of Egypt and cultivated in Iran, Iraq, Afghanistan, Pakistan and India. TA has a great medicinal and nutrition values because its seed extract consists of carbohydrates (—CHO, —OH), glucosides (6-O-β-glucopyranosyl oxythymol), oleoresin, saponin, phenols, volatiles (thymol, γ-terpinmene, para-cymene, α- and β-pinene, dipentene), proteins, fat, fibres, and minerals (P, Fe, Ca, etc). Furthermore, prominent principle oils such as, carvone (46%), dillapiole (9%) and limonene (38%) along with reducing agents (nicotinic acid), are also present in TA. Therefore, due to the presence of these biochemical ingredients, TA can be served as the reducing and capping agent without addition of any external stabilizing agent, during the synthesis process of NPs.

Silver has long been famous for its good inhibitory effect towards many bacterial strains/microorganisms and catalytic activity. Therefore, commonly used in medical and industrial products that directly come in to the contact with the human body, such as shampoos, soaps, detergent, shoes, cosmetic products, and toothpaste, besides photocatalytic and pharmaceutical applications. Moreover, superiority of the nanosilver particles over other candidates of the same class is already established in terms of the small losses in optical frequency during the surface-plasmon propagation, high conductivity and stability at ambient conditions, less costlier price than other noble metals such as gold and platinum, high primitive character, and wide range of visible light absorption, etc. Which, prompt us to select silver as a plasmonic material for this study. Tiny nano-particles of the noble metals with localised spin plasmonic resonance (LSPR) are known as plasmonic material. Free electrons integrated with the photon energy produces a LSPR [28–32] on exposing nano-particles of noble metals to sunlight. Therefore, NPs of the noble metals will be act as the active centres on catalyst for the thermal redox reaction that can trap, scatter, and concentrate light [33–35], due to the fast charge transfer and result in enhanced activities.

Pure Ag NPs, as well as some chemically modified Ag NPs has also been in trend that to be used in various applications such as: cleaning water, catalyst, sensor, optoelectronic properties, eradication of organic pollutants, etc. Out of which removal of organic pollutants (nitrophenols) from waste water is very important. 4-Nitrophenol (PNP) is a highly stable and low water-soluble chemical that used to be found in waste water that produced by explosive- and dye-industries. Environmental Protection Agency of United States rated nitrophenols highly polluted chemical among the top 114 organic pollutants. It adversely affects the human and animal organs like liver, kidney, blood and central nervous system, skin, etc [36]. Moreover, the degradation of PNP to nondangerous product is difficult due to its high stability. Therefore, the study for catalytic reduction of hazardous PNP to benign 4-aminophenol (PAP) becomes a remarkable step in terms of nitrophenol-pollution mitigation [37]. PAP is very fascinating chemical as it can be used in production of analgesic and antipyretic drugs, photographic developer, corrosion inhibitor, anti-corrosion lubricant, and many more applications. It can be produced by reduction of PNP to PAP in sodium borohydride at room temperature. Aforementioned reaction is a thermodynamically feasible process as it involves E^0 for PNP/PAP $= -0.76$ V and $H_3BO_3/BH_4^- = -1.33$ V versus NHE. But this reaction is kinetically restricted by nature and never produce PAP as end product but generate an intermediate i.e. *p*-nitrophenolate ion in absence of the catalyst. Metal NPs or modified metal NPs, were used to catalyse the above reaction. Few prominent e example, Ag NPs-decorated Polyaniline nanofibers (AgNPs/PANINFs) nanocomposites [38], SiO_2-coated graphene oxide nanosheets, decorated with Ag nanoparticles [39], Pd/CuO NPs [40], synthesized by using of *Theobroma cacao* L. seed extract, etc, were used for catalytic reduction of PNP into PAP in presence of excess of $NaBH_4$. The metal NPs can serve as catalysts to transfer electrons from ion to the PNP. Both absorbed on the catalyst surface and result in the production of PAP.

Hence, this study is devoted to the fabrication of the Ag NPs by biogenic reduction method using aqueous TA seed extract at ambient condition. Consequently, as-synthesized Ag NPs were rigorously investigated using advance techniques i.e. XRD (X-ray diffraction), UV–vis spectrophotometry, FTIR and ATR spectroscopy, scanning electron microscopy (SEM) and their corresponding energy dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), photoluminescence emission (PLE), cyclic voltammetry and electrochemical impedance spectroscopy (EIS), etc. Finally, the biogenic Ag NPs were used to reduce *p*-nitrophenol to *p*-aminophenol in excess of $NaBH_4$ and reaction mechanism for this reaction is also suggested. Effect of aging/particle size on catalytic activity and rate of reaction will also be discussed.

2. Results and discussion

2.1. Crystallography of Ag NPs

The powder XRD patterns of the Ag NPs exhibited the major diffraction peaks at 37.554°, 43.751° 64.021° and 76.949° (Fig. 1).

One sharp and strong peak at 37.554°, followed by the other small peaks can be index by (111), (200), (220) and (311) planes of a cubic crystal system (a = 4.0686 Å) that matched well with the standard JCPDS card No. 04-0783 of pure silver. These results attributed to the orientation of the crystal growth along the 111 plane. Peak broadening noticed in XRD data of the silver nanoparticles was dedicated to the small particle size and spin plasmonic resonance phenomena. No bogus Bragg reflections were observed in the pattern due to crystallographic impurities in the sample, which reflected the presence of the 100% pure silver metal in the sample [41]. Ag NPs was crystallized in face centered cubic symmetry of the space group Fm-3m (Space group number: 225) and point group m3m. Debye Scherrer equation

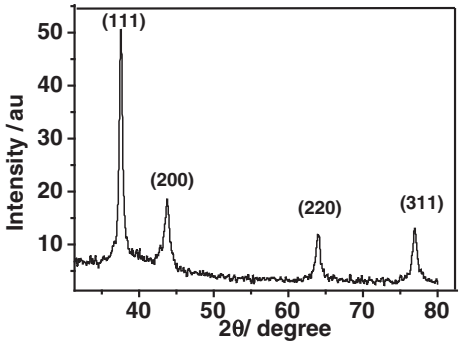

Fig. 1. XRD pattern of biogenic TA supported Ag NPs with reference to the standard JCPDS file No. 04-0783 of pure Ag.