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Evaluation of the kinetic and catalytic properties of biogenically synthesized silver nanoparticles

Manoj Kumar Choudhary [a, b, c, *], Jyoti Kataria [b], Shweta Sharma [c, **]

[a] Nanomaterial Research Laboratory, Department of Chemistry, Guru Nanak National College, Doraha, Ludhiana 141421, Punjab, India
[b] P.G. Department of Chemistry, Panjab University Research Centre, GGDSD College, Sector 32-C, Chandigarh 160030, India
[c] Institute of Forensic Science and Criminology, Panjab University, Chandigarh 160014, India

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ABSTRACT

Present work encompasses the facile green and biogenic preparation of silver nanoparticles (AgNPs) using of cumin seeds (*Cuminum cyminum*) extract. The phytochemicals present in seeds extract, possessing strong anti-oxidant potential, reduce silver (Ag^{+}) ions and subsequently stabilize the newly formed silver (Ag^{0}) nuclei. The effect of pH, concentration of seeds extract, reaction time and stability of nanoparticles were investigated by UV–visible spectroscopy. The reddish-brown color at a wavelength of 422 nm corresponding to surface plasmon resonance (SPR) absorption, confirmed the formation of AgNPs. Further, the nucleation, growth and stabilization phases have been examined. The rate constant value suggests the rapid formation of stable AgNPs. The nanoparticles were further investigated by X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM) and Fourier transform infrared (FT-IR) spectroscopy. The biosynthesized AgNPs had been observed to be spherical in shape with an average particle size of 16 ± 2 nm as calculated from TEM images. Furthermore, the stable AgNPs were excellent nanocatalysts towards borohydride reduction of various anthropogenic dye pollutants *viz.* methylene blue (MB), methyl red (MR), rhodamine-B (Rh-B) and 4–nitrophenol (4–NP).

1. Introduction

Silver nanoparticles (AgNPs) due to their distinctive properties such as surface plasmon resonance (SPR), high stability and biocompatibility etc. (Burda et al., 2005; Daniel and Astruc, 2004), have shown remarkable alluring properties in the field of optical, electronic, biological and medical science. Tailoring of size, shape and surface properties can lead to adjustable transformations in their optical properties (Kelly et al., 2003; Liz-Marzán, 2006), thus, enhancing the applications in manufacturing of optical gadgets (Nallathamby et al., 2008), bioimaging (Erathodiyil and Ying, 2011), sensing (Guo et al., 2015; Karthiga et al., 2016; Wang et al., 2010), catalysis (Liu and Zhao, 2009), and surface enhanced Raman scattering (SERS) (Preciado-Flores et al., 2011) etc.

For the facile preparation of colloidal nanoparticles, the wet-chemical synthesis, includes reduction of metal ions through chemical reducing agents followed by polymer or surfactant supported stabilization (Sun and Xia, 2002). The organic polymeric or surfactant molecules serve as effective capping agents to prevent the aggregation of nanoparticles. However, excess usage of various hazardous organic reagents in wet-chemical preparation has raised alarm regarding the consequences of chemically prepared metal nanoparticles on the living individuals and the ecosystem. Further, these organic molecules may make insulating layers around the particles, affecting the efficacy of metal nanoparticles. To overcome the negative impacts of wet-chemical methods, researchers have integrated “green chemistry” principles in the metal nanoparticles synthesis using plant materials (Augustine et al., 2014; Basu et al., 2015; Choudhary et al., 2016, 2017; Gaddala and Nataru, 2015; John et al., 2015; Sumi Maria et al., 2015; Vankar and Shukla, 2012). A naturally benevolent solvent and eco-friendly reducing and stabilizing agents are the fundamental components for the green synthetic process. In the past decades, research groups are working in the direction of using biological systems such as microorganisms (bacteria, fungi, etc.) and plants for the fabrication of metal nanoparticles. The utilization of plant matter for synthesis of

* Corresponding author. Nanomaterial Research Laboratory, Department of Chemistry, Guru Nanak National College, Doraha, Ludhiana 141421, Punjab, India.
** Corresponding author.
E-mail addresses: choudhary.nrl@gmail.com (M.K. Choudhary), 25shweta@pu.ac.in (S. Sharma).

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nanoparticles on large scale, have gained significant attraction over the use of microorganisms due to various factors such as (i) simple operating procedures (ii) quick or timely scalability (iii) exclusion of cell culture maintenance. Plant materials including, leaves, roots, bark, flowers, fruits and seeds have numerous secondary metabolites with proficient anti-microbial (Purkayastha et al., 2012), anti-proliferative (Rani and Meena, 2014), and anti-oxidant activities (Marinova et al., 2013). These phytoconstituents synergistically reduce metal ions and protect the metal nuclei from coagulation. Though, literature reports the different mechanisms of formation of noble metal nanoparticles (MNPs) (Ahmad and Sharma, 2012; Nazeruddin et al., 2014; Nesakumar et al., 2016), the kinetics for biogenic formation of MNPs has not been discussed, so far.

In the present work, green biomimetic synthesis of AgNPs has been endeavored using aqueous extract of *Cuminum cyminum* seeds, commonly known as cumin seeds. Cumin is a herbaceous flowering plant, belonging to the *Apiaceae* family. The major phytochemical available in the cumin seeds include polyphenols, flavonoids, saponins, tannins and coumarins etc. (Aljuhaimi and Ghafoor, 2013; Johri, 2011; Rani and Meena, 2014). The effect of pH, concentration of seeds extract, reaction time, and kinetics of AgNPs formation has been deliberated through UV–visible spectroscopy. The stable biogenic nanoparticles were characterized using sophisticated analytical techniques i.e. XRD, FT-IR and HR-TEM. The nanoparticles have further been explored as efficient nano-catalysts for the borohydride reduction of four mutagenic pollutants such as methylene blue (MB), methyl red (MR), rhodamine-B (Rh-B) and 4–nitrophenol (4–NP).

2. Experimental

2.1. Materials and methods

Glassware was thoroughly cleaned with aqua regia and washed with double distilled water. Cumin seeds were purchased from local market of Doraha, Punjab, India. Silver nitrate ($AgNO_3$) was acquired from RENKEM, India, while all other chemicals including dyes (MB, Rh-B, MR and 4–NP) were obtained from Merck and employed without further refinement.

2.2. Preparation of AgNPs

The biogenic synthesis of AgNPs was detailed in our previous study (Choudhary et al., 2016). Briefly, 5 g of washed and dried seeds were refluxed in 100 ml of double distilled water for 60 min and cumin seeds extract (CSE) was filtered twice using Whatman No. 1 filter paper and stored at 4 °C. To optimize the amount of seeds extract required for biosynthesis of AgNPs, varying volumes (0.5–3.0 ml) of aqueous CSE was added to the required amount of 1 mM aqueous solution (to make total volume 10 ml) of silver nitrate at pH 10. The synthesis mixture was agitated at 25 °C on a magnetic stirrer under dark conditions and monitored visually for variation in color from pale yellow to reddish brown and periodically with UV–visible spectrophotometer. The amount which showed the narrow intense band and shortest wavelength for SPR absorption was selected as optimum.

The effect of pH on biosynthesis of AgNPs had been optimized by maintaining the precursor solution of $AgNO_3$ at 4, 7 and 10 pH, respectively. The pH value favoring the intense and narrow SPR absorption band was chosen as optimized pH for subsequent experiments. Further, to investigate the effect of aging on the stability of synthesized AgNPs, an aliquot of nanoparticles solution was diluted and stored in 5 ml glass vial at room temperature for 3 months.

2.3. Instrumentation

UV–vis absorption spectra were obtained in the range of 200–700 nm using a double beam, T-90+ UV–visible spectrophotometer (PG Instruments, UK) with 10 mm quartz cell. TEM images were acquired by G^2 20 TWIN high resolution transmission electron microscope (FEI, TECNAI), operating at 200 kV. The Infrared spectra were recorded using RX-I FT-IR spectrophotometer (Perkin Elmer, USA). The aqueous colloidal solution of AgNPs was centrifuged at 6000 rpm for 10 min. The pellet was re-dispersed in distilled water. The centrifugation process and re-dispersion was repeated thrice to assure better segregation of uncoordinated molecules from the nanoparticle surfaces. XRD pattern was obtained using X'Pert-Pro X-ray diffractometer using Cu Kα monochromatic radiation (1.5406 Å) operating at 45 kV and 40 mA.

2.4. Catalytic efficacy of biosynthesized AgNPs

The biogenically synthesized AgNPs were investigated at room temperature, for their ability to act as potential catalysts. The borohydride reduction of four model pollutants i.e. MB, MR, Rh-B and 4–NP was carried out to investigate the catalytic efficacy of biosynthesized AgNPs. Initially, a 30 ml AgNPs solution was centrifuged and washed thrice with double distilled water and ethanol, respectively. The pellet found at the bottom of tube was re-dispersed ultrasonically in 30 ml of double distilled water to make AgNPs solution free from phytoconstituents. The catalytic reduction of each of these pollutants was analyzed by recording their UV–visible spectrum. The reduction of dye pollutants was also examined without $NaBH_4$ and AgNPs.

3. Results and discussion

3.1. Biosynthesis of AgNPs

Cuminum cyminum seeds used for the synthesis of AgNPs represented as a natural biosynthetic material. The active biomolecules of cumin seeds played dual role of reducing and capping agent in the fabrication of highly stable AgNPs. On addition of aqueous extract of *C. cyminum* to the solution of silver nitrate, a rapid change in color from pale yellow to reddish brown at room temperature was observed on agitation for 10 min. The color became more intense with the progression of reaction w.r.t. time. The observed variation in color of the solution can be ascribed to SPR vibrations of the AgNPs (Mulvaney, 1996). The reaction procedure depicting the biochemical reaction between $AgNO_3$ and aqueous seeds extract, resulting in the formation of AgNPs is shown in Fig. 1.

3.2. Effect of pH on biosynthesis of AgNPs

Fig. 2a displays the UV–visible absorption spectra taken after 60–80 min of reaction for biogenic AgNPs synthesized using cumin seeds extract at different pH (4, 7 and 10). The spectra revealed a considerable difference in pattern. The SPR absorption band at pH 10 was the most intense and narrow. At lower pH, broadening and slight red shift of peaks were observed, which can be ascribed to aggregation or uneven shapes of particles at low pH (Alqadi et al., 2014). Since the resonance stabilized phenoxy radicals of polyphenolic acids are responsible for the capping of Ag^0 nuclei (Choudhary et al., 2017), the aggregation of AgNPs at low pH results from weak interactions between Ag^0 nuclei and phenolic -OH groups.

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