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Catalytic degradation of organic dyes using biosynthesized silver nanoparticles

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ABSTRACT

The green synthesis of metallic nanoparticles paved the way to improve and protect the environment by decreasing the use of toxic chemicals and eliminating biological risks in biomedical applications. Plant mediated synthesis of metal nanoparticles is gaining more importance owing to its simplicity, rapid rate of synthesis of nanoparticles and eco-friendliness. The present article reports an environmentally benign and unexploited method for the synthesis of silver nanocatalysts using *Trigonella foenum-graecum* seeds, which is a potential source of phytochemicals. The UV–visible absorption spectra of the silver samples exhibited distinct band centered around 400–440 nm. The major phytochemicals present in the seed extract responsible for the formation of silver nanocatalysts are identified using FTIR spectroscopy. The report emphasizes the effect of the size of silver nanoparticles on the degradation rate of hazardous dyes, methyl orange, methylene blue and eosin Y by $NaBH_4$. The efficiency of silver nanoparticles as a promising candidate for the catalysis of organic dyes by $NaBH_4$ through the electron transfer process is established in the present study.

1. Introduction

The development of nanotechnology has become an important issue for scientific exploration in physics, chemistry and engineering. In this context metal nanoparticles present some distinct features that are directly related to particle size and shape. Metal nanoparticles especially silver nanoparticles are found suitable candidates in applications such as medical diagnosis (Jain et al., 2008), drug delivery systems (Elechiguerra et al., 2005), sanitization (Krishnaraj et al., 2010), water treatment (Li et al., 2008) and wound healing (Tian et al., 2007). Currently, sustainability initiatives that use green chemistry to improve and protect our global environment are becoming focal issues in many fields of research. This has paved the way for the greener synthesis of nanoparticles and has proven to be promising due to slower kinetics, better manipulation, control over crystal growth and their stabilization. This has motivated an upsurge in research on the synthesis routes that allow better control of shape and size for various nanotechnological applications. Instead of using toxic chemicals for the reduction and stabilization of metallic nanoparticles, the use of various biological entities has received considerable attention in the field of nanobiotechnology. Among the many possible natural products, biologically active plant products represent excellent scaffolds for this purpose (Dubey et al., 2010a,b; Roopan et al., 2013). Among the various categories of compounds in plants that have potential biological activities, phytochemicals are emerging as an important natural resource for the synthesis of metallic nanoparticles. They play important roles in both reduction and stabilization of nanoparticles.

The focus of the present work is to apply the factual principles of green chemistry in the synthesis of silver nanoparticles by using stand alone reducing and capping agent as *Trigonella foenum-graecum* seeds with water as a solvent. Fenugreek is an annual herb whose leaves and seeds are widely consumed in Indo-Pak sub continent as spice and medicine. Fleiss reported that fenugreek seeds are used as galactagogue by nursing mothers to increase inadequate breast milk supply (Fleiss, 1988). The diseases such as diabetes and hypercholesterolemia can be treated using fenugreek seeds (Basch et al., 2003; Miraldi et al., 2001). It is also reported that fenugreek seeds exhibit pharmacological properties such as antitumor, antiviral, antimicrobial, anti-inflammatory, hypotensive and antioxidant activity (Cowan, 1998; Shetty and Labbe, 1998). The synthesis method in the article is unique on its own till date. This article reveals the possibility of producing highly monodispersed, stable and colloidal silver nanoparticles.

Dyes are a major class of synthetic organic compounds released by many industries such as paper, plastic, leather, food, cosmetic, textile and pharmaceutical industries (Kulkarni et al., 1985; Zollinger, 1987). These effluents result in significant environmental pollution. Azo dye compounds were recognized as potential carcinogens (Chung and Cerniglia, 1992; Kusic et al., 2006). Abatement of dyes is a required part of wastewater treatment. The dye effluents

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are highly resistant to microorganisms so that their reduction by using conventional biological treatment is generally ineffective and also resistant to destruction by physical–chemical treatments in a high effluent concentration. Nanotechnology has been extended to the wastewater treatments in the recent years. Due to high surface area silver nanoparticles exhibits an enhanced reactivity (Kang et al., 2000). In the present study, we have investigated the size dependent catalytic degradation of organic dyes – methyl orange, methylene blue and eosin Y by $NaBH_4$ in the presence of silver colloids.

2. Materials and methods

Silver nitrate (99.99%), methyl orange, eosin Y, methylene blue and sodium borohydride were procured from sigma Aldrich. All glasswares were cleaned with aqua regia and rinsed several times with de-ionized water.

2.1. Preparation of extract

T. foenum-graecum seeds were purchased from local market. 10 g of *T. foenum-graecum* seeds was washed using deionised water several times and boiled with 100 mL of deionised water at 373 K for 2 min. The extract was filtered and used for further experiments.

2.2. Synthesis of silver nanoparticles

Silver nanoparticles (sample F_1) have been synthesized by adding 2 mL extract to preheated 30 mL 3.1×10^{-4} M silver nitrate solution and boiled at 373 K for 2 min. The formation of silver nanoparticles is indicated by the appearance of yellowish brown color within 5 min. Samples F_2–F_5 were synthesized in the same procedure by adding 5 mL, 8 mL, 10 mL and 15 mL extracts, respectively.

2.3. Catalysis

1 mL 100 mM sodium borohydride solution is added to 1 mL 10^{-3} M methyl orange (MO), methylene blue and eosin Y, respectively. The solutions are then made up to 10 mL using deionised water and vigorously stirred for 5 min. Then 0.5 mL, 2 mL and 2 mL of silver colloid (sample F_1) is added to the solutions, respectively, and stirred for five more minutes. The degradation of dyes is indicated by the decolorisation of the solution.

Methylene blue initially blue in color in an oxidizing environment became colorless in the presence of reducing agent ($NaBH_4$) indicating the reduction of methylene blue to leucomethylene blue (LMB) (Leonard et al., 2011).

The effect of size variation on the degradation of dyes has been investigated by performing the catalytic experiments using samples F_3 and F_5. The reaction unsupported by the catalyst is a studied as a reference. All the degradation process was monitored using UV–visible absorption spectrophotometer.

3. Characterization

UV–visible spectra analysis was performed for all samples and the absorption maxima were analyzed at a wavelength of 200–700 nm using Lambda35 PerkinElmer Spectrophotometer. Deionised water was used for background correction of all UV–visible absorption spectra. All samples were centrifuged several times using deionised water and loaded in a 1 cm path length quartz cuvettte for sampling. FTIR spectra of nanocrystalline sample and extract were recorded using IR Prestige-21 Schimadzu spectrometer. XRD pattern was recorded by XPERT-PRO diffractometer using Cu Kα radiation (λ = 1.5406 Å). The scanning was performed in the region of 2θ from 20 degrees to 90 degree. The morphology of the silver nanoparticles was examined using Tecnai G^2 30Transmission Electron Microscope. The size dependent catalytic action of as prepared samples was examined by monitoring the UV–visible spectra of the samples at a regular interval of 1 min after adding the colloid.

4. Results and discussion

A well-accepted scientific consensus emanating from several scientific investigations is that fenugreek seeds contain high levels of antioxidant polyphenols, including flavanoids (Sumayya et al., 2012). The phenolics and other phytochemicals in the extracts not only result in effective reduction of silver salts to nanoparticles but their chemical framework is also effective at wrapping around the nanoparticles to provide excellent robustness against agglomeration. The discovery of the unique chemical power of non-toxic phytochemicals in nanoparticles formation is of paramount importance in the context of the production of silver nanoparticles for medical and technological applications under non-toxic conditions.

The phytochemical analysis of fenugreek seeds reveal the presence of carbohydrates, proteins, phenols, sterols, flavanoids, alkaloids, quinones, terpenoids, tannins, glycosides, saponins in the fenugreek seed (Sumayya et al., 2012). Phenolic compounds possess hydroxyl and carboxyl groups, which are able to bind to metals (Harborn, 1988). The roots of many plants contain high levels of phenolic compounds which may inactivate ions by chelating. According to Moran et al. (1997) the chelating ability of phenolic compounds is related to the high nucleophilic character of the aromatic rings. Also, the excellent antioxidant activity of flavanoids resides mainly in their ability to donate electrons or hydrogen atoms.

The protein present may cap the silver nanoparticles formed, restricting the agglomeration of the particles and thus checking the size and shape (Ahmad et al., 2010). Presumably biosynthetic products or reduced cofactors play an important part in the reduction of ions to silver nanoparticles as the concept of antioxidant action of phenol compounds is not new.

4.1. UV–visible spectra

The strong interaction of metal nanoparticles with light results in the collective oscillation of the conduction electrons on the metal surface, known as a surface plasmon resonance (SPR). The SPR results in unusually strong scattering and absorption properties. Due to the unique optical properties of silver nanoparticles, a great deal of information about the physical state can be obtained by analyzing the spectra. As the diameter increases, the peak plasmon resonance shifts to longer wavelengths and broadens. The secondary band may be due to a quadrupole resonance that has a different electron oscillation pattern than the primary dipole resonance. The band wavelength, the band width, and the effect of secondary resonances yield a unique spectral fingerprint for a plasmonic nanoparticle with a specific size and shape. The UV–visible absorption spectra of samples F_1–F_5 is shown in Fig. 1. The spectra reveal a strong dependence of absorbance on the quantity of extract added. The spectra exhibits absorption bands in the range 400–440 nm. The broad SPR can be attributed to the formation of anisotropic particles. The spectra reveal a secondary band in higher wavelength as the quantity of extract increases. For non-spherical metallic nanoparticles, the surface plasmons are unevenly distributed which results in the shape dependent SPR absorption spectra (Sun and Xia, 2003). According to Mie's theory small