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Effects of cationic and anionic micelles on the morphology of biogenic silver nanoparticles, and their catalytic activity for congo red

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ABSTRACT

The effects of cationic and anionic micelles of cetyltrimethylammonium bromide (CTAB) and sodiumdodecyl sulphate (SDS) have been studied on the morphology of biogenic Ag-nanoparticles (Ag-NPs) using an aqueous extract of *Mentha* leaves extract as a reducing agent for the first time. UV–visible absorption spectra showed one surface Plasmon resonance peak (SPR) at ca. 425 nm, indicating the Ag-NPs formation having almost spherical morphology. Reaction-time profiles suggest that rates (nucleation and growth) of the Ag-NPs were completed within the 30 min of the reaction time. Extract-, CTAB-, and SDS-capped Ag-NPs were characterized by conventional TEM, SEM and EDX techniques. CTAB and SDS have significant impact on the as prepared Ag-NPs. Absorbance continuous decreases, and decreases-increases with these stabilizers, respectively. Resulting Ag-NPs was used as a catalyst to the removal of congo red from industrial wastes water. UV–visible absorption spectra indicate that congo red form stable complex with Ag-NPs.

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1. Introduction

It is well known that nano-biotechnology and nano-toxicology are the most dynamic inter disciplinary areas of research in contemporary material science where by plants and other natural recourses have a significant role in the synthesis of biogenic coated advanced nanoparticles [1–3]. Bakshi and his coworkers determined the biological applications of protein and enzyme coated metal nanoparticles from hemolytic and antimicrobial studies and demonstrated their potential uses in pharmaceutical and food industries [4–6]. Various green chemical reduction methods have been used for the synthesis of Ag-NPs in the absence and presence of dissimilar stabilizers (surfactants [7], peptides [8], carbohydrates [9], proteins [10], polymers [11], lipids [12], and plants extract [13]. Jose-Yacaman et al. reported a simple green biosynthetic method to the formation of gold and silver nanoparticles using living plants and/or its extract as reducing agents for the first time [14,15]. These investigators pointed out that experimental conditions (nature of reducing agent, pH, capping action of stabilizers, and mixing order of reactants over stabilizers) play an important role during the nucleation processes. Out of these stabilizers, cetyltrimethylammonium bromide (cationic surfactant) acted as a shape-directing agent during the growth of anisotropic advanced nano-materials of silver and gold.

Mentha spicata leaves have been and are extensively used as herbal medicines all over the world and commonly called as spearmint that belongs to the family Lamiaceae. The aromatic leaves of mint are used fresh and dried as flavorings or spices in a wide variety of foods. Mint possesses antimicrobial, antiviral, antitumor, and antioxidant properties due to the presence of various water soluble and water insoluble reactive constituents like carvone, caffeic acid, cineole, limonene, luteolin, menthone, menthol, α-pinene, β-pinene, rosmarinic acid, etc. [16–20]. Fecka and Turek used chromatographic techniques for the quantitatively estimation of various water-soluble polyphenolic compounds (eriocitrin, luteolin 7-O-rutinoside, luteolin 7-O-glucuronide, lithospermic acid, rosmarinic acid, and methyl rosmarinate) from commercial *Mentha* [20,21].

Due to a broad spectrum of applications of silver and its nanoparticles in the field of analytical, medicinal and nano-chemistry, synthesis of advanced nano-materials has been the subject of various investigators by using the biosynthetic methods [7,8,22]. However, the roles of surfactants in the extra cellular green biosynthesis of biogenic silver sol are not yet known. It was, therefore, thought to be of interest to determine the morphology, role of surfactants, rates of nucleation processes, and other kinetic data related to the green synthesis of Ag-NPs using an aqueous extract of *Mentha* leaves with and without surfactants. For this purpose, two different surfactants, namely cetyltrimethylammonium bromide and sodiumdodecyl sulphate were chosen. Incidentally, this study appears to be the first report regarding the effects of surfactants on the morphology of *Mentha* leaves extract assisted Ag-NPs. In addition, catalytic activity of as prepared Ag-NPs towards the degradation of congo red (diazo dye industrial wastes) was also determined and discussed.

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2. Experimental

2.1. Mint extract preparation and chemicals

Mint was purchased from the local market. The leaves were separated and washed under tap water. 10 g of mint leaves were chopped into fine pieces and added in 100 cm^3 double distilled deionized water, heated at 60 °C for 30 min, cooled, and filtered using Whatman filter paper No.1. The filtrate was used as a reducing and/or capping agent for the synthesis of Ag-NPs. All glassware was washed with aqua regia (3:1 HCl and HNO_3), rinsed with water, and drying before use. Silver nitrate ($AgNO_3$, BDH, 99.99%), congo red ($C_{32}H_{22}N_6Na_2O_6S_2$; formula weight = 696, Sigma), surfactants (cetyltrimethylammonium bromide and sodiumdodecyl sulphate, Fluka) and other reagents were used without further purification. Molecular structures of congo red, CTAB, and SDS are given in Scheme 1.

2.2. Instruments

UV–visible spectral analysis provides preliminary information about the size, shape, and the size distribution of the metal nanoparticles due to the appearance of one or several surface resonance plasmon peaks in the entire visible region of the spectra. Therefore, spectra of the silver sols were measured at different time intervals (5 min, 10 min, 20 min, 30 min) between wave lengths of 200 to 700 nm in a spectrophotometer (UV-160v, Shimadzu, Japan), having a resolution of 1 nm. Transmission electron microscopy (TEM) technique was used to visualize the morphology of the Ag-NPs. The high-resolution transmission electron microscope (TECHNAI-320 KV JAPAN), operating at 200 kV was used to determine the morphology. TEM grids were prepared by placing few drops as prepared Ag-NPs solution on carbon-coated copper grids and drying under open air at room temperature.

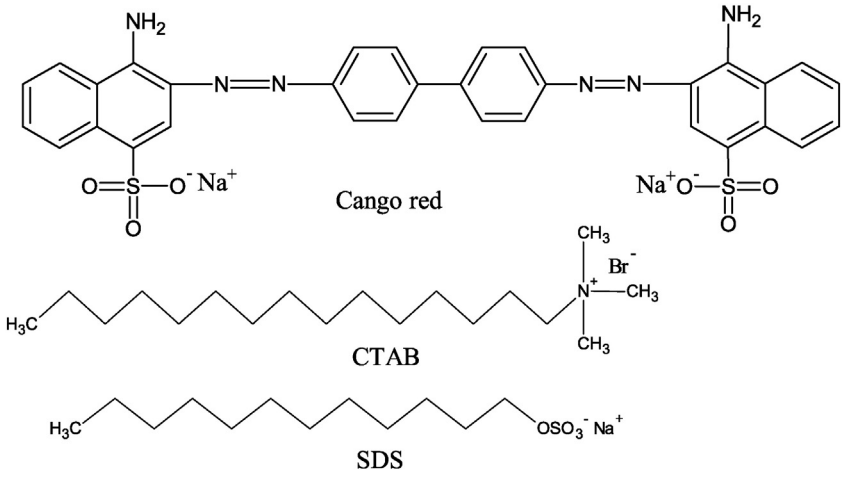
2.3. Synthesis and kinetics of Ag-NPs

In a typical experiment, aqueous $AgNO_3$ solution (0.01 mol dm^{-3}; 5 cm^3) was added in a two-necked 250 cm^3 reaction flask containing *Mentha* leaf extract (5 cm^3) + required [CTAB or SDS] for reduction of Ag^+ ions into the metallic Ag^0. The reaction flask was then kept for some time in dark at room temperature to avoid photo activation of Ag^+ ions. As the reaction time increases, the color change of the mixture from pale light, yellowish brown to finally reddish brown, indicating the formation of Ag-NPs. In order to confirmed the complete reduction of Ag^+ to Ag^0, NaCl solution (0.01 mol dm^{-3}; 10 cm^3) was added into the colloidal brown colored silver sols. We did not observed the appearance of any type of turbidity or white precipitate, which clearly suggests that the Ag^+ ions have been converted into the Ag^0 [23]. Progress of the was followed by recording the spectra of the silver sols formation at different time intervals at 425 nm against blanks containing all reagents except oxidant. Apparent first rate constants were calculated from the initial part of the slopes of the plots of ln (a/(1 − a)) versus time by a fixed time method [24].

3. Results and discussion

3.1. UV–visible spectra

It has been established that UV–visible spectra provides preliminary information about the morphology of metal nanoparticles [25]. For silver nanoparticles, the appearance of sharp plasmon band observable at ca. 400 nm is the most characteristic part of the UV–visible spectra of silver sols [26]. Therefore, to determine the morphology of as prepared Ag-NPs, a series of kinetic experiments were carried out under different experimental conditions, and their spectra were recorded at different time intervals. The observed results are summarized in Figs. 1 to 5. Our absorption spectra consist a sharp peak at 425 nm in the whole visible region (350–700 nm), which might be due to the formation of spherical Ag-NPs. As the reaction-time increases, a blue shift was observed from 425 nm to 400 nm, the width of the band has also increased, which might be due to the excitation of different multiple modes present in faceted and anisotropic growth of particles [27]. We point out that changes occurred in the position of peak with time (Fig. 1), support the formation of only sphere-shaped Ag-NPs. On the other hand, increasing intensity of the surface plasmon band at ca. 425 nm with time, indicating the formation of additional different size nanoparticles and/or aggregation of small nano-size particles. To see the role of [Ag^+] on the nucleation rate of AgNPs formation, the effect of [Ag^+] was studied at fixed [extract] (5.0 cm^3). The [Ag^+] varied from 4.0×10^{-4} to 40.0×10^{-4} mol dm^{-3}. The observed results are summarized in Fig. 2 as absorbance-time profiles. Interestingly, absorbance was found to be directly proportional to the [Ag^+], suggesting the nucleation and growth paths involved in the formation of Ag-NPs. As can be seen in Fig 2 (typical example), the new Ag-NPs were not formed after the first 20 min of the reaction. We did not observed any significant change after a certain reaction time, indicating that the nucleation might be finished. The optical images of the reactants (mint leaves, and their aqueous extract), and formation of Ag-NPs after the addition of $AgNO_3$ into the extract are summarized in Scheme 2 (flow diagram showing the systematic step-wise presentation to the formation of Ag-NPs from the leaves to extract and finally to the silver sols).



Scheme 1. Molecular structures of congo red, CTAB and SDS.

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