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Effect of pH on photosynthesized silver nanoparticles using *Dianthus caryophyllus* L. (Carnation) flower

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Abstract : In this paper, silver nanoparticles (AgNPs) were synthesized using the flower extract of *Dianthus caryophyllus* L. (carnation) where extract acted as both reducing and stabilizing agent. The effect of pH (4, 6, 9 and 10) on the synthesis route of AgNPs was analysed. Their absorption spectra were recorded through UV-Visible spectrophotometer in terms of the absorption peaks (400 and 440 nm).Inverse correlation was observed between the pH values and size of AgNPs synthesized in the reaction mixture. At pH 4, there was no significant colour change in the solution which indicated the absence of any AgNPs in the mixture. At relatively higher pH, the more spherical and smaller AgNPs were recorded as compared to low pH values. The resultant AgNPs were characterized using UV-Visible spectrophotometer and Transmission electron microscope (TEM) techniques. **Keywords :** Silver nanoparticles, Green synthesis, *Dianthus Caryophyllus* flower, pH variation.

Introduction

Nano-size particles are unique in itself due to their relatively large surface to volume ratio as compared to their bulk materials, which makes their chemical, physical and optical property so unique. During recent years, this uniqueness led to many research on metallic nanoparticles and their applications like catalysts, optical sensors, antibacterial activity, data storage capacity, optoelectronics^{1,2}. Silver has been acquiring much more research centric approach due to its wide set of applications in almost every field. Numerous methodologies have been reported to synthesize stable AgNPs. One of the main consideration in the process is to synthesis the clean, non-toxic, eco-friendly and cheaper silver nanoparticles. Chemical and physical methods for the synthesis of AgNPs, followed over the decades, are found to be more complex, expensive and involve the usage of various toxic chemicals. Green synthesis of AgNPs gives a new platform to this problem.

In the present research work an attempt was made to synthesis AgNPs using *D.Caryophyllus* flowers. Carnation flowers itself have various medicinal and therapeutic values which can be used to enhance the effectiveness of AgNPs. The significance of medicinal plants in the discovery of new set of therapeutic agents for drug delivery is already known, over the years. The carnation flowers have been reported to possess strong medicinal properties which are traditionally being used in treating nervous and gastro-intestinal disorders, throat and gum infections, cancerous tumors, $etc^{3,4,5,6}$. This flower has also been traditionally used as alexiteric, antispasmodic, cardiotonic, nervine, and antiviral^{6,7}. Medicinal bioactive substances of this flower can easily synthesize large amount of AgNPs with more efficient pharmaceutical drug-based abilities. In order to maximize the use of nanosize AgNPs, many research has been focused to control their size and shape⁸. The difference in shape and size is because of various physical and chemical factors like temperature, pH, humidity and so on⁹. Many researchers have studied the change in the shape and size of AgNPs due to varying pH value

of the solution where high pH corresponded to much smaller AgNPs in comparison to low pH based synthesized AgNPs^{10,11}. It has been observed that at very high pH (>11) values, the spherical shape of AgNPs was lost¹². Hence, a suitable optimum condition is required in order to obtain desired shaped and sized AgNPs.

Materials and methods

Materials

Silver nitrate, Sodium hydroxide, Hydrogen chloride (from Hi-media, India and Sigma chemicals company, USA) and *Dianthus caryophyllus* L. (carnation) flowers from D P flower shop, Faridabad, Haryana (28.4211 N 77.3078 E).

Green synthesis of AgNPs

The flower petals of carnation was properly washed and sundried for about 10 days in order to remove the unwanted impurities and interacting volatile flower components. These dried petals were finely crushed and about 1 g of them was boiled with 10 ml distilled water for 20-25 min. The boiling process was necessary to release the cellular content of the flower which acted as both reducing and stabilizing agent in the synthesis process. The flower extract was then filtered through Whatman filter paper 1 and stored at 4°C for further use.

The production of AgNPs was done successfully by mixing 4 mM AgNO₃ and 2% (v/v) diluted aqueous flower extract under incubation (40 °C, 180 rpm) for 24 hours. After confirming the production of AgNPs using UV-Visible spectrophotometer, then the effect of pH (4, 6, 9 and 10) was investigated on the production process.

Characterizations

The resultant AgNPs were subjected to UV-Visible spectrometer (PC based Double Beam Spectrophotometer, Systronics 2202) and Transmission electron microscope,Hitachi (H-7500) for the characterization.

Results and discussions

UV-Visible spectrophotometer was used to obtain the information about the surface plasmon response of AgNPs by recording its absorption spectra. About 4 mM AgNO₃ and 2% (v/v) diluted aqueous flower extractunder incubation (40 °C, 180 rpm) for 24 hours at pH 9.5 was found suitable to synthesis AgNPs. A sharp and narrow UV-Visible spectra peak appeared at 414 nm indicating the uniform and smaller AgNPs (Fig1).

The effect of pH was investigated on the production process of AgNPs using UV-Visible spectroscopy and TEM. The absorption spectra at various pH values (4, 6, 9 and 10) were recorded. It was observed that the surface plasmon resonance shifted towards the shorter wavelength as pH values were increased. There was no production of AgNPs for pH 4 as no visible change in the colour of the reaction mixture was observed even up to 36 hours. As the pH of reaction was increased from 6, 9 and 10, the deep yellow colour appeared in the mixture indicating the successful production of AgNPs with their respective absorption peaks at 440, 420 and 399 nm(Fig 2).

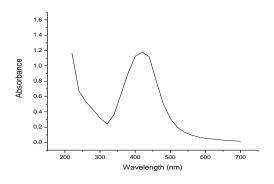


Fig. 1 UV-Visible spectra of AgNPs

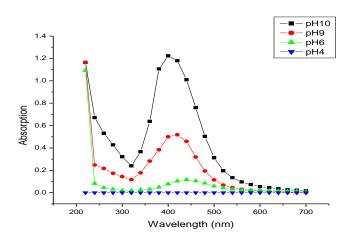


Fig. 2 UV-Visible spectra of AgNPs at pH (6, 9 and 10)

TEM technique was used to analyse the morphology and size of the resultant AgNPs. Inverse corelation between the change in size of AGNPs and pH values used was observed through TEM images (Fig 3). At pH 6, the irregular and overlapped AgNPs were seen which may be due to the poor balance between growth rate and nucleation process of AgNPs. The size of the resultant AgNPs at pH 9 and 10, was found in the range 10-30 nm and 7-20 nm. Higher values of pH were attributed towards the more spherical and smaller AgNPs.

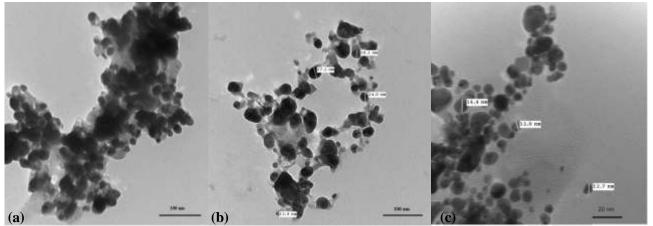


Fig. 3 TEM images of AgNPs at various pH values: (a) pH 6 (b) pH 9 and (c)pH 10

Conclusion

Green synthesis of colloidal AgNPs was carried out using *D.caryophyllus* L. flower extract in which flower extract acted as both reducing and stabilizing agent in the reaction mixture. The biological reduction of 4 mMAgNO₃ was done successfully using 2 % (v/v) aqueous flower extract under the incubation of 40 °C at 180 rpm up to 24 hours with varying pH (4, 6, 9 and 10). The appearance of deep yellow colour confirmed the formation AgNPs. The surface plasmon peak of the solution was between 400 and 440 nm, confirming the characteristics of AgNPs, was analysed using UV-Visible spectrophotometer. The effect of pH values on the absorption peak of the reaction mixture was clearly seen with increase in pH, the plasmon peak shifts to the left or to the lower wavelengths indicating the formation of smaller AgNPs.

TEM images of different pH valued AgNPs also showed the inverse corelation between their size and pH values. As pH of the reaction is increased, the size of AgNPs was reduced as compared to the respective low pH value.

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