Biosynthesis of Silver Nanoparticles Using *HoneySuchle Flowers* Extract and Their Application for Reductive Catalysis of Direct Violet 1

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Abstract. Biosynthesis of silver nanoparticles (AgNPs) using *HoneySuchle Flowers* Extract as reducing and stabilizing agent has been discussed in this paper, and AgNPs have been characterized by UV-Vis spectroscopy, DLS analysis, TEM and EDS analysis. The surface plasmon resonance (SPR) peak of AgNPs was observed at around 429 nm, and the average particles size of AgNPs was around 50 nm. The biosynthesis temperature had great impact on the particle size distributions of AgNPs and thereby affected the catalytic characteristics of AgNPs for the reductive degradation of Direct Violet 1 by NaBH\textsubscript{4}. The results showed that increasing of AgNPs particle size was upon the increasing of reaction temperature, which was adverse to catalytic reactivity of AgNPs.

1. Introduction
Silver nanoparticles (AgNPs) have been widely used in catalytic[1-3], optic[4], electronic[5], and other applications[6-8] due to their unique properties. The green synthesis method, including in bottom to up approach, has obvious advantages over physical and chemical methods. The use of plants as the production assembly of AgNPs has drawn great attention, because of its rapid, ecofriendly, non-pathogenic, economical protocol and providing a single step technique for the biosynthetic processes. A large number of plants are reported to facilitate AgNPs syntheses with different sizes and shapes[9].

Synthetic organic dyes are extensively used in various industries such as textile, paper, plastic etc. The discharges from these industries result in substantial environmental pollution[2]. It is a well-known fact that AgNPs and theirs composites show greater catalytic activities in the area of dye reduction and their removal. Bogireddy et al.[10] synthesized AgNPs using Sterculia acuminata fruit extract, and biofabricated AgNPs showed great catalytic efficiency for the reduction/degradation of various dyes.

In this study, we aimed at develop a green process for the synthesis of AgNPs by *HoneySuchle Flowers* extract as reducing and stabilizing agent. The biosynthetic AgNPs were characterized by UV-visible spectroscopy, DLS with zeta potential, TEM and EDS analysis. In order to evaluate the catalytic property of AgNPs, catalytic reduction Direct Violet 1 was carried out in the presence NaBH\textsubscript{4}. AgNPs prepared in different temperatures were compared on the reductive catalytic abilites, and the paper also discussed the factors affecting the catalytic abilities of the AgNPs. Meanwhile, we report for the first time the degradation of Direct Violet 1 by NaBH\textsubscript{4} as reducing agent in the presence of AgNPs.
2. Materials and Methods

2.1. Materials
The experimental material HoneySuchle Flowers extract was purchased from Shanxi Sciphar Natural Products Co., Ltd. Silver nitrate (AgNO₃), NaOH and NaBH₄ were received from Aladdin Industrial Corporation and were used without purification. Direct Violet 1 (Figure 1.) was sourced from Zhejiang Run Tu Co. Ltd. The ultrapure water was used for the preparation of experimental solutions.

![Chemical structure of Direct Violet 1](image)

Figure 1. Chemical structure of Direct Violet 1.

2.2. Biosynthesis of AgNPs
Exactly 10 mL of AgNO₃ (0.01 mol/L) was added to 89 mL distilled water, and 1.0 mL of HoneySuchle Flowers extract solution (5.0 g/L) was added in a drop wise manner in continuous stirring condition to the AgNO₃ solution. No chemicals were added to the reaction solution except for the adjusting of pH value using NaOH (0.05 mol/L), and the solution was heated by water bath under different temperatures (25, 45, 65 and 85°C) within 40 mins.

2.3. Characterization of AgNPs
UV-Vis analysis was conducted using a UV-3600 spectrophotometer (Shimadzu, Japan) for the evaluation of AgNPs formation in the solution. Transmission electron microscope (Tecnai G220 FEI, USA) was performed to visualize the size and morphology of biosynthesized AgNPs, and the TEM-energy dispersive X-ray (EDAX, USA) analysis was also performed to verify the presence of silver element. DLS analysis was used for the measurement of average particle size distribution and zeta potential of AgNPs by a Zetasizer Nano series instrument (Malven, UK).

2.4. Catalytic degradation of Direct Violet 1
The degradation of Direct Violet 1 was conducted in a 4.0 mL quartz cuvette. 2.0 mL of Direct Violet 1 (100 mg/L) was blended with 0.1 mL sodium borohydride (0.2 mol/L) and 0.05 mL AgNPs. The catalytic degradation process was determined by measuring UV-Vis absorption spectra of Direct Violet 1 at intervals of 3 mins.

3. Results and Discussion

![Molecular structure of chlorogenic acid](image)

Figure 2. Molecular structure of chlorogenic acid.

The green synthesis of AgNPs was effectively performed using HoneySuchle Flowers extract, and silver nitrate as the precursor. No other hazardous or toxic chemicals were used in the synthesis process. According to the information provided by the manufacturer, the main content of HoneySuchle Flowers extract is chlorogenic acid (CGA) (98%) which is shown in Figure 2. Among naturally occurring bioactive compounds, CGA is a polyphenol compound in plants, which can be utilized for reducing silver ions (Ag⁺) to silver metal (Ag⁰) nanoparticles. Similar results have been reported for
the phytosynthesis of AgNPs by Terminalia cuneata[11], tea leaf extract[12], grape seed extract[13], Cassia auriculata flower extract[14], et al.

3.1. Characterization of AgNPs
As the addition of *HoneySuchle Flowers* extract to the silver nitrate solution, the color of mixed solution converted gradually from light green to dark brown in a few minutes, which indicated the formation of AgNPs in the solution. UV-Vis absorption spectroscopy is a common tool to verify the existence of AgNPs in the aqueous solution, and the absorption spectrum of AgNPs is affected by several factors, such as particle size, shape and the local chemical environment. Therefore, the AgNPs solution prepared at 25°C was tested by UV-Vis spectrometer. Figure 3 shows the UV-Vis absorption spectrum of the synthesized AgNPs, and the absorption peak of AgNPs locates as 429 nm, which is due to the SPR absorption of AgNPs[15].

![Figure 3. UV-visible spectrum of AgNPs synthesized by *HoneySuchle Flowers* extract.](image)

The biosynthesized AgNPs were subjected to further investigation by TEM together with EDAX. When using TEM, the AgNPs were observed under different magnification powers, and the pictures (Figure 4) clearly revealed the surface morphology of AgNPs. It is visible from the TEM images that the AgNPs exhibit a typical spherical and an ellipsoidal morphology. The particle size distribution of AgNPs in the solution was directly determined by DLS measurements. The average size of the AgNPs is around 40 nm, and the zeta potential of stable AgNPs is calculated as -26.9 mV suggesting the high stability of AgNPs[11]. As shown in Figure 4, TEM results reveal clearly that the AgNPs are capped
with biomolecules from HoneySuchle Flowers extract, which confirmed the stabilizing effect for HoneySuchle Flowers extract in the phytosynthesis of AgNPs.

The presence of zero-valent silver is confirmed by using EDAX analysis, and the EDS pattern of AgNPs is shown in Figure 5. The spectrum shows a 3 keV peak correspond to Ag, which confirms the successful phytosynthesis of AgNPs.

3.2. Effects of synthetic temperature on AgNPs

Figure 6 shows the characteristic SPR peaks at 429, 426, 421, and 417 when the AgNPs were synthesized at temperature of 25, 45, 65 and 85°C. In addition, it was also observed that, when the reaction temperature was increased, the intensities of the SPR bands also increased, which indicates that a higher yield of AgNPs was obtained at higher temperature. The AgNPs synthesized at temperature of 25, 45, 65 and 85°C were marked as DT1, DT2, DT3 and DT4.

![Figure 6. UV-visible spectra of AgNPs synthesized at different temperatures (A 25°C, B 45°C, C 65°C and D 85°C).](image)

![Figure 7. Particle size distributions of different AgNPs synthesized by HoneySuchle Flowers extract: (a) DT1, (b) DT2, (c) DT3, (d) DT4.](image)

DLS was used to look into the size distribution aspects of the silver nanoparticles. Figure 7 depicts the extent of size distribution against the intensity of light scattering and number for AgNPs synthesized at different temperatures. From the results, the calculated average particles size of AgNPs is 38 nm to 68 nm when the reaction temperature increases from 25°C to 85°C. The increment in the
particle size was attributed to an increased reduction rate at high temperature which further enhanced the size of the nanoparticles.

3.3. Reductive degradation of Direct Violet 1 by AgNPs
Direct Violet 1 is an azo dye, and it is non-biodegradable by means of conventional wastewater treatment method. Direct Violet 1 show strong absorbance peaks at 532 nm and 308 nm as shown in Figure 8. The $\lambda_{\text{max}}$ value at 532 nm is due to the absorbance of two $-\text{N=N-}$ groups in Direct Violet 1, which is the characteristic absorption peak of Direct Violet 1. Since the $\lambda_{\text{max}}$ of Direct Violet 1 is well separated from the surface plasmon absorption of AgNPs, the absorbance at 532 nm was used to observe the degradation of the dye.

![Figure 8. Degradation of Direct Violet 1 using different catalysts: (a) No AgNPs, (b) DT1, (c) DT2, (d) DT3, and (e) DT4.](image)

The reductive degradation of Direct Violet 1 was very limited by NaBH$_4$ alone (Figure 8(a)). This showed that Direct Violet 1 could not be degraded solely by NaBH$_4$. With the addition of AgNPs (DT1, DT2, DT3 and DT4) to the solution containing Direct Violet 1 and NaBH$_4$, an immediate decrease occurred and then continued till the reaction of 18 min. This was accompanied by the concomitant appearance and growth of new peaks at 273 nm and 241 nm (Figure 8(b, c, d, e)), which might be the results of new organic compounds generation during the reductive degradation of Direct Violet 1. The trend was also visually confirmed with colour change from deep violet to faint yellow. In the end of the reaction, a weak absorption was observed at 392 nm. This is believed to be the SPR band of nano silver catalyst.

The degradation of Direct Violet 1 is mainly because of nanoparticle-mediate transfer electrons. After adding the nanocatalyst, the borohydride ion which donates the electrons and Direct Violet which accepts the electrons gets adsorbed on the surface of the nanocatalyst. The reduction occurs by the transfer of electrons from borohydride ions to Direct Violet 1. AgNPs help this electron shuttling process by relaying electrons from the donor to the acceptor. The blue special shift of the SPR band of AgNPs is because of the nanoparticle surface alteration, arising due to the "electron relay" process.
Furthermore, AgNPs synthesized at different temperatures showed different catalytic activities as shown in Figure 9(b-d). The descent rate of characteristic absorption peak of Direct Violet 1 decreased when the synthesis temperature increased 25-85°C. This should be associate with the weaker catalytic activity of AgNPs with bigger sizes and less surface areas when they were synthesized at higher temperatures.

Based on the previous research work[16], it is suggested that in the degradation of Direct Violet 1 by NaBH₄ in the presence of biogenic AgNPs, the simultaneous cleavages of two azo bonds occur resulting in the formation of corresponding Benzidine and Sodium 1,2-diamino-8-hydroxy-5-naphthalenesulfonate as shown in Figure 9.

![Figure 9. Degradation mechanism of Direct Violet 1.](image_url)

### 3.4. Calculation of the reaction kinetics of Direct Violet 1

In order to evaluate the degradation kinetics for the reactions, the pseudo-first order equation with respect to Direct Violet 1 is used due to the relatively high concentration of NaBH₄. The reaction kinetic can be expressed as the following equation:

\[
\ln \frac{A}{A_0} = -kt
\]

where \( k \) is the pseudo-first order rate constant, \( t \) is the reaction time, \([A_0]\) is the absorbance of the peak at 532 nm at time \( t = 0 \), and \([A_t]\) is the absorbance at time "t" at the wavelength of 532 nm. The relationships between \( \ln(A_t/A_0) \) and time for the reduction of Direct Violet 1 using different AgNPs catalysts are shown in Figure 10.

![Figure 10. \( \ln(A_t/A_0) \) vs. time linear fits during the degradation of Direct Violet 1.](image_url)

A linear relationship was obtained in all cases confirming the pseudo-first order nature of the reaction. Bases on the linear regression of \( \ln(A_t/A_0) \) versus time, the rate constants and degradation percentages were calculated and listed in Table 1. The rate constant decreased from 0.1161 min⁻¹ (DT1)
to 0.0556 min⁻¹ (DT4), and degradation percentage also decreased from 87.30% (DT1) to 70.92% (DT4). AgNPs synthesized at higher temperature exhibited lower catalytic activity, which could be related to the formation of bigger AgNPs at higher reaction temperature.

Table 1. Results of rate constants and percentage of degradation.

| AgNPs | Reaction temperature | Average particle size | First order constant | Direct Violet 1 degradation after 18 min |
|-------|----------------------|-----------------------|----------------------|----------------------------------------|
| DT1   | 25 °C                | 37.72 nm              | 0.1161 min⁻¹         | 87.30%                                 |
| DT2   | 45 °C                | 38.05 nm              | 0.1062 min⁻¹         | 84.40%                                 |
| DT3   | 65 °C                | 52.18 nm              | 0.0868 min⁻¹         | 80.53%                                 |
| DT4   | 85 °C                | 68.53 nm              | 0.0556 min⁻¹         | 70.92%                                 |

4. Conclusions
This paper presented a green way for the preparation of AgNPs by *HoneySuchle Flowers* extract. The formation of AgNPs was initially confirmed by UV-Vis spectroscopy analysis, and an obvious SPR peak was observed in the spectrum. As shown in the TEM images, the AgNPs were mainly spherical morphology, and the EDS spectrum verified the existence silver element in the nanoparticles. The average diameter of AgNPs were around 50 nm in the medium reaction temperature. The AgNPs showed excellent catalytic activity in the reduction/degradation of Direct Violet 1 using NaBH₄ as reducing agent. The higher the reaction temperature, the larger the size and slower the reaction rate.

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6. References
[1] Edison T J I, Sethuraman M G, 2012 *Process Biochemistry* 47(9) 1351
[2] Joseph S, Mathew B, 2015 *Materials Science and Engineering: B* 195 90
[3] Li P, Li S, Wang Y, et al., 2017 *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 520 26
[4] Pathrose B, Nampoori V P N, Radhakrishnan P, et al., 2016 *Optik-International Journal for Light and Electron Optics* 127(7) 3684
[5] Jimenez-Villacorta F, Climent-Pascual E, Ramirez-Jimenez R, et al., 2016 *Carbon* 101 305
[6] Guo D W, Dou D D, Ge L, et al., 2015 *Colloids and Surfaces B: Biointerfaces* 134 229
[7] He H W, Tao G, Wang Y J, et al., 2017 *Materials Science and Engineering C* 80 509
[8] Mohanty A S, Jena B S, 2017 *Journal of Colloid and Interface Science* 496 513
[9] Borase H P, Salunke B K, Salunkhe R B, et al., 2014 *Applied Biochemistry and Biotechnology* 173 1
[10] Bogireddy N K R, Kumar H A K, Mandal B K, 2016 *Journal of Environmental Chemical Engineering* 4 56
[11] Edison T N J I, Lee Y R, Sethuraman M G, 2016 *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 161 122
[12] Sun Q, Cai X, Li J W, Zheng M, et al., 2014 *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 444 226
[13] Xu H, Wang L, Su H Y, et al., 2014 *Food Biophysics* 10 12
[14] Muthu K, Priya S, 2107 *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 179 66
[15] Varadavenkatesan T, Selvaraj R, Vinayagam R, 2016 *Journal of Molecular Liquids* 221 1063
[16] Yao P, Zhang J, Xing T L, et al., 2018 *Journal of Industrial and Engineering Chemistry* 58 74