Article

Dye Sequestration Using Biosynthesized Silver Nanoparticles Adsorbent in Aqueous Solutions

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Abstract: Nanomaterials have gained much attention in the field of environmental remediation, largely due to their high surface area-to-volume ratio and other unique physical, chemical, and biological characteristics that emerge due to its size effects. Metallic nanoparticles are traditionally manufactured using wet chemical processes; however, the chemicals utilized are generally hazardous and combustible. The biosynthesis of nanoparticles using a variety of plant resources is considered a green technology because it does not use toxic chemicals. This work focuses on the green synthesis of biogenetic silver nanoparticles and their use in the sequestration of colorants from aqueous solution. The extract of aquatic macrophyte Salvinia molesta (water hyacinth) has been employed to prepare silver nanoparticles by chemical reduction reaction. In the UV-visible spectrum of the synthesized silver nanoparticles, the absorbance peak was detected in the 420–430 nm range. The synthesized silver nanoparticles were used to sequester methylene blue (MB) dye in aqueous solution. About 121.04 mg/g was found as the highest adsorption capacity of methylene blue dye on the silver nanoparticles according to the Langmuir isotherm. It was observed that the experimental results and the pseudo-second order kinetics are in good agreement. As a result, the biosynthesized silver nanoparticle might be a potential adsorbent material in the field of environmental rehabilitation and cleanup.

Keywords: silver nanoparticles; green synthesis; adsorption; colorants; methylene blue dye

1. Introduction

Textile production requires a large quantity of water and energy. Factories create a large amount of contaminated water after finishing dyeing and completing their products [1]. Due to its huge volume and nature, this water is regarded to be extremely dangerous for human beings. There are a number of environmental problems associated with discharging dyeing waste water directly into the environment. Waste water has a potential effect to cause serious damage to aquatic life, soil, and drinking water [2]. Furthermore, some dyes and their tailing-remained products have the potential to be carcinogenic and poisonous. As a result, the dyes must be removed before disposal. A wide range of techniques have been explored to treat wastewater, including biodegradation and ultrafiltration as well as photocatalytic degradation, oxygenation, and adhesion. When it comes to the treatment of these dye-containing effluents, traditional adsorption is a very low-cost and effective method [3]. The physicochemical characteristics of the adsorbent determine the efficiency of any adsorption procedure. The search for novel adsorbents with large specific surface area, high adsorption capacity, and a quick adsorption rate, as well as unique surface reactivity, is therefore highly essential and useful [4].
Nanotechnology allows the creation of nanomaterials that may be used for a variety of scientific and technical purposes. As a result of nanotechnology, new nanomaterials may be used for a variety of applications with a measurement of less than 100 nanometers [5]. Research on nanoparticles has received increased attention in recent years, owing to a wide range of essential uses in health and different environmental issues. As a result of their tiny size, nanoparticles have a higher surface-to-volume ratio or a greater surface area per weight than larger particles, making them more reactive to interact with other molecules. Silver nanoparticles (AgNPs) are more important than other noble metal nanoparticles due to their specific features, such as excellent optical property, electrical conductivity, oxidative property, antibacterial activity, and catalytic activity. Silver nanoparticles are traditionally produced using hazardous chemicals and at a high cost. The utilization of environmentally friendly resources such as plant leaf extract, microorganisms, and enzymes may be employed for the biological production of nanoparticles, which offers several environmental benefits. The green production of nanoparticles is critical for the treatment of many hazardous compounds that cannot be addressed chemically [6]. The fabrication of nanoparticles using chemical methods are time-consuming and have a high production cost. Therefore, scientists were particularly interested in the creation of nanoparticles by green production methods.

In the literature, researchers fabricated silver nanoparticles and applied for different applications. Vanaja et al. (2014) prepared silver nanoparticles using *Morinda tinctoria* leaf extract under specific pH conditions and further characterized by different spectroscopic techniques [7]. They concluded that the size as well as the quantity of silver nanoparticles formed are strongly dependent on the pH, and basic pH supports the biosynthesis of silver nanoparticles, whereas no silver nanoparticles were detected in the acid medium. Silver nanoparticles were prepared with sizes ranging from 79 to 90 nm and applied for photo catalytic activity of MB degradation [8]. Anu Kumar et al. (2016) experimented with a simple and non-hazardous method for synthesizing silver Nano catalyst by using *Viola serpens* leaf extract [9].

The biosynthesis of AgNPs mainly involves three main steps: (1) solvent medium should be selected, (2) environmentally friendly reducing agents are selected, and (3) nontoxic substances are chosen for the AgNP’s stability. When a substrate of low value is used by living cells to produce higher-value products, this device is called a bioreactor [10]. Plant parts act as a bioreactor for the expression in tissues remote from the penetration of ion sites, with the capability to reduce metal ions on the surface. The plant has a strong hyperaccumulation capacity of metal ions, which is a tool for the bioaccumulation of metal oxide-NPs. The whole plant can be used for nanoparticle fabrication, whereas size and shape of NPs mainly depends upon parts of the plant. Biogenic fabrication by plant extracts have been used in the production of AgNPs and found interesting owing to size, surface area, structure, and unique properties. There are several disadvantages of physical and chemical methods of nanometal fabrication, as they need to use biogenic synthesis methods, which are economically feasible and ecofriendly [11]. The purpose of this work is to synthesize AgNP using the aquatic weed, *Salvinia molesta*, as a reducing agent and assess their effectiveness in sequencing MB dye, which is commonly used in the textile industry. It was shown that the synthesized AgNPs by plant extracts adsorb and quickly decrease the concentrations of the MB dye, both in terms of catalysis and kinetics [12].

### 2. Materials and Methods

#### 2.1. Materials

Silver nitrate and methylene blue (MB) dye were purchased from Sigma Aldrich. *Salvinia molesta*, a macrophyte kariba weed, is an aquatic fern and native to southeastern Brazil [13]. Its observed as a free-floating plant that remains on the surface of water. The leaves are 0.1–4 cm long, with a bristly surface caused by the hair-like strands and were collected from riverbanks and ponds in the summer of 2021 (see Figure 1).
The collected *S. molesta* was washed many times in warm distilled water to remove any dust or other impurities. A total of 50 g of *S. molesta* leaves were cleaned and finely chopped before being placed in 500 mL beakers containing 200 mL of double-distilled water. The mixture was allowed to boil for 1 h at 100 °C. The obtained solution mixture was then cooled to room temperature [14]. The leaf extracts were filtered by using Whatman number 41 filter paper.

2.2.2. Silver Nanoparticle (AgNPs) Synthesis

In order to synthesize AgNPs, an aqueous solution of silver nitrate was prepared using double-distilled water. AgNPs were made by mixing 1 mM silver nitrate solution with *S. molesta* leaf extract and continuous stirring at 300 rpm for 72 h at room temperature using a magnetic stirrer. The formation of AgNPs is indicated by the appearance of a yellow-brown color after 8 h of agitation and turns reddish brown after 72 h of agitation in the dark [15,16]. The resulting suspension of silver nitrate and *S. molesta* extract were centrifuged at 15,000 rpm for 15 min. To remove silver ions and seed extract residue, the pellet containing AgNPs was washed three to four times with deionized water. Biosynthesized AgNPs were lyophilized after being precipitated. To further characterize, the lyophilized nanoparticles were stored in a cool, dry, and dark environment.

2.2.3. Characterization of Biogenic AgNPs

The mixture of silver nitrate and *S. molesta* extract solution were taken in different ratios (1:1, 1:2, 1:3, and 1:4), and the UV-visible spectra of AgNPs at different ratios were obtained using a UV-1800 Shimadzu spectrophotometer. Silver nanoparticle morphology was studied using a lyophilized sample of AgNPs using a scanning electron microscope (SEM) operating at 20 kV. Transmission electron microscopy (TEM) working at an acceleration voltage of 200 kV was used to determine the morphology and size of biosynthesized AgNPs. The crystalline structure of the biogenic nanoparticles was determined using a pattern of selected area electron diffraction (SAED).

2.2.4. Dye Adsorption and Sequestration Using AgNPs Adsorbate

For the sequestration of MB dye, batch studies were carried out in a 250 mL conical flask containing 50 mL of dye solution. The effects of initial dye concentration (10–100 mg/L), equilibrium time, pH (2–10), and temperature (30–45 °C) were investigated. After adding a desired amount (0.1 g) of AgNPs to MB dye solution, the mixture was stirred at 200 rpm with a magnetic stirrer at an ambient temperature for equilibrium time. After equilibrium time, the solution was filtered to separate pellet and supernatant [17–21]. The collected supernatant was analyzed using UV-Vis spectrophotometer at a maximum
wavelength of 660 nm to measure the MB dye concentration in the residual solution. The efficiency of decolorization (%) has been calculated by using the following Equation (1) [10]:

\[
\text{Decolorization} (%) = \left( \frac{C_0 - C_1}{C_0} \right) \times 100\%
\]

where \(C_0\) is the initial concentration of dye and \(C_1\) is the concentration of dye after irradiation in the selected time interval.

3. Results and Discussion
3.1. Characterization of Biosynthesized AgNPs

Silver nanoparticles were synthesized by the addition of Salvinia molesta extract to the AgNO\(_3\) solution. In the AgNO\(_3\)/Salvinia molesta solution, silver nanoparticle synthesis is indicated by a progressive color change from colorless to yellow to reddish brown, as shown in Figure 2. Surface plasmon vibration, an optical characteristic found only in noble metals, is responsible for this color change [22]. Further, UV-visible spectroscopy has been used to confirm the formation of silver nanoparticles in aqueous solution. The solution was scanned over a range of wavelength as 300–800 nm. Biogenic AgNPs have a prominent peak absorbance at 430 nm [23], which is typical, as shown in Figure 3. *Salvinia molesta* leaf extract generated highly dense AgNPs, as shown by SEM examination in Figure 4. The acquired morphology demonstrated that the produced AgNPs were virtually spherical. The particles appear agglomerated because the presence of several significant bio-organic chemicals extruded from the leaves appear as a chelating agent that stabilizes the produced AgNPs in solution. A similar phenomenon was reported by Ranjith kumar et al. (2018) [24].

![Figure 2](image2.png)

**Figure 2.** Color change during AgNPs biosynthesis at different time intervals.

![Figure 3](image3.png)

**Figure 3.** UV spectra of the biosynthesized AgNPs using different ratios of silver nitrate to *S. molesta* leaves extract.
A High-resolution transmission electron microscopy (HRTEM) investigation was carried out to characterize the surface morphology and size (Figure 5a–c). The average particle size was determined to be 1 nm. Additionally, the particles were rounded and well-dispersed, suggesting the presence of capping peptides around each particle that help stabilize the nanoparticles. For a face-centered cubic structure, the SAED patterns recorded for a single particle in the aggregates corresponded to a characteristic polycrystalline ring pattern as shown in the Figure 5d [25]. The bright circular ring observed is due to the reflection from the lattice planes of crystalline biosynthesized AgNPs.

Figure 4. SEM image of the biosynthesized AgNPs.

Figure 5. (a–c) TEM image and (d) SAED diffraction pattern of the biosynthesized AgNPs.

3.2. Effect of Dye Concentration on the Adsorption Process

Adsorption processes are depending on the initial concentration of adsorbate. Initially, a large number of surface-active sites will be available for adsorbing the desired dye molecules. So, the adsorption is fast at the initial stage. Figure 6 shows the effect of time and concentration of the investigated MB dye with respect to decolorization percentage. A decrease in degradation efficiency occurs as dye concentration increases due to several factors. As there are fewer active sites on the surface, hydroxyl radicals will be less active, and the probability of a photon reaching the surface of AgNPs is decreased with increasing the dye concentration, resulting in a decreased decolorization percentage [26].
Figure 6. Effect of time on the decolorization percentage of methylene blue dye adsorbed on the biosynthesized AgNPs.

3.3. Effect of pH on the Adsorption Process

Each of the adsorbate solutions were prepared at different pH levels (2.0, 4.0, 6.0, 8.0, and 10) using either 1.0 N HCl or 1.0 N NaOH. There were optimum amounts of adsorbents in dye solutions that were added (0.1 g of AgNPs), and the mixture was agitated. The amount of dye that was adsorbed was measured. From the plot of pH versus percentage of dye removal (Figure 7), it was observed that the optimum pH of the process was 4. This is due to the fact that the degradation of MB dye was increased. The neutralization of the negative charges at the surface of AgNPs will enhance the diffusion phenomena to occur, and more active sites will be available for the adsorption process. However, when the pH is below 4, the dye degradation and the number of negatively charged adsorbent sites decreases. The increasing in the number of positively charged surface active sites enhances the dye-adsorbent repulsion, which reduces the efficiency of the adsorption process. At a lower pH, the MB adsorption dye improved due to the acidic media. As pH increases, the adsorbent surface acquired negatively charges, and they are responsible for increasing the adsorption capacity due to the electrostatic interaction. However, the adsorption of MB dye was observed decreasing at high pH.

Figure 7. Effect of pH on the decolorization percentage of the methylene blue dye adsorbed on the biosynthesized AgNPs.
3.4. Effect Temperature on the Adsorption Process

An initial MB dye concentration of 10 mg/L was used to determine the effect of temperature on degradation efficiency of MB on the surface of the biosynthesized AgNPs. Figure 8 exhibits the influence of temperature on percentage decolorization. According to the study, the optimal temperature for dye degradation was found to be 35 °C. Further, when the temperature was raised above 35 °C, the dye adsorption decreased significantly. This is due to the fact that the adsorptive forces at the adsorbent active sites and the adsorbate may be weakened.

![Figure 8](image-url)

**Figure 8.** Effect of temperature on the decolorization percentage of the methylene blue dye adsorbed on the biosynthesized AgNPs.

3.5. Adsorption Isotherms

The interaction between adsorbate and adsorbent is described using adsorption isotherms. Langmuir and Freundlich isotherm models are used to assess experimental and theoretical MB dye adsorption data. According to Langmuir, adsorption occurs uniformly or homogeneously on the surface of the biosynthesized AgNPs adsorbent. Langmuir’s linear expression can be found in Equation (2) [10];

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q}$$  \hspace{1cm} (2)

where \(C_e\) is the equilibrium concentration of a dye in solution (mg/L), \(q_e\) is the amount of dye adsorbed on to the Cs (mg/g) MB, \(Q\) is the Langmuir constant related to adsorption capacity (mg/g), and \(b\) is the Langmuir constant related to sorption energy (L/mg). The experimental data for the decolorization of MB dye is fitted in the rearranged Langmuir equation, which has found successful applications of monolayer adsorption. The plot obtained is shown in Figure 9. A Freundlich isotherm is used to determine the adsorption capacity of MB dye on the biosynthesized AgNPs adsorbent. Equation (3) is the linear form of the Freundlich isotherm.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (3)

where \(C_e\) is the equilibrium concentration of the dye in solution (mg/L), \(q_e\) is the amount of dye adsorbed on the adsorbent (mg/g), and \(K_f\) and \(1/n\) are Freundlich constants [27]. The graph of \(\log q_e\) is plotted against \(\log C_e\) and is found not to be linear as shown in Figure 10. The \(1/n\) value from the experimental data is greater than 1, which shows unsatisfactory adsorption of MB dye onto the surface of the biosynthesized AgNPs adsorbent. The parameters of Langmuir and Freundlich constants are given in Table 1. The Langmuir isotherm was found to be the best fit in the experimental data—better than the Freundlich
isotherm. This shows the monolayer adsorption of MB dye onto the biosynthesized AgNPs adsorbent, with the maximum adsorption capacity of 1.023 mg/g.

![Figure 9](image_url) **Figure 9.** Decolorization percentage of the methylene blue dye as adsorbed on the biosynthesized AgNPs. (Fitted with the Langmuir model).

![Figure 10](image_url) **Figure 10.** Relationship between log \( q_e \) with log \( C_e \) of the adsorbed methylene blue dye on the biosynthesized AgNPs.

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### 3.6. Adsorption Kinetics

For the study of adsorption kinetics, pseudo first order and pseudo second order kinetic models are widely used. These models are used to determine the rate at which adsorption occurs or the rate at which solute is absorbed. When it comes to designing the reactors, these models pay more attention. Our study examined the rate at which MB dye adsorbed onto surfaces by applying pseudo first- and second-order equations in order to determine how fast it adsorbed. There is a strong correlation between experimental data and predicted values using different models (value close or equal to 1).
3.6.1. Pseudo First Order Kinetic Model

The rate of MB dye adsorption on the biosynthesized AgNPs adsorbent’s surface is proportional to the amount of dye adsorbed from the liquid phase; the pseudo first order kinetic equation may be expressed as in Equation (4) [10]:

$$\log q_e - q_t = \log q_e - \frac{k_{ad} t}{2.303}$$ (4)

where \(q\) and \(q_e\) represent the amount of dye adsorbed (mg/g) at time \(t\) and at equilibrium time, respectively, where \(k_{ad}\) is the adsorption rate constant [28]. Figure 11 shows the plot of linearized form of the pseudo first order kinetic model. The slopes and intercepts of the plotted graph of \((\log q_e - q_t)\) versus time were used to determine the pseudo first order rate constant \(k_{ad}\) and the equilibrium adsorption capacity \(q_e\).

![Figure 11](image)

Figure 11. Pseudo first order kinetic model of the adsorption process of methylene blue dye on the biosynthesized AgNPs.

3.6.2. Pseudo Second Order Kinetic Model

The pseudo second order kinetics model can be expressed by Equation (5) [10]:

$$\frac{dq_t}{qt} = k_2(q_e - q_t)^2$$ (5)

where \(k_2\) represents the pseudo second order rate constant. The \(q_e\) and \(q_t\) represent the amount of dyes adsorbed (mg/g) at equilibrium and at time \(t\). For the boundary condition \(t = 0\) to \(t = t\) and \(q_t = 0\) to \(q_t = t\), the integral form of the Equation (3) becomes Equation (6) [10]:

$$\frac{t}{q_t} = 1/k_2q_e^2 + t/q_e$$ (6)

The values of \(k_2\) and \(q_e\) are calculated from the intercepts and slopes of the plots of \(t/q_t\) vs. time (Figure 12), and the corresponding coefficient of determined \(R^2\) values are listed in Table 2. The experimental value of \(q_e\) is 10 mg/L and the theoretical value is 9.708 mg/L for second order. From this reason, it can be interpreted that the adsorption process of methylene blue dye on the biosynthesized AgNPs follows second order kinetics [29–31].

<table>
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<th>Pseudo First Order</th>
<th>Pseudo Second Order</th>
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<tr>
<td>(q_e) (mg/g)</td>
<td>(k_{ad}) (1/min)</td>
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As a result of these findings, the prepared nanoparticles mediated by *S. molesta* could be used effectively in environmental remediation, and their phenomenal behavior might be extensively utilized to breakdown hazardous organic colorants from different industrial effluents. The pseudo first order (P.F.O) reaction $R^2$ value was calculated as 0.91 as compared to pseudo second order (P.S.O) reaction 0.99 and fitted well. Decolorization percentage of methylene blue dye as adsorbed on the AgNPs was fitted with the Langmuir model.

### 4. Conclusions

This study highlights the use of nanotechnology for methylene blue dye adsorption on biosynthesized silver nanoparticles with effective results. It was shown that bioactive components of the aquatic macrophyte (*S. molesta*) extracts can be used as a reducing agent to fabricate silver nanoparticles used efficiently in methylene blue dye adsorption. This is a quick method for the production of well-defined silver nanoparticles, as evidenced by UV-Vis, TEM, SEM, and SAED methods. The efficient activity of silver nanoparticles enhancing the methylene blue dye degradation was observed. The biosynthesized Ag-NPs have high adsorption activity against the decolorization of methylene blue dye. The present study could be an indication for further future research to identify other nanoparticles for different synthetic dyes for efficient degradation potential.

**Author Contributions:** Conceptualization M.B., W.M.D. and M.K.H.; Methodology, M.B., W.M.D. and M.K.H.; formal analysis, M.B., W.M.D. and M.K.H.; investigation, M.B., W.M.D. and M.K.H.; resources, M.B., W.M.D. and M.K.H.; writing original draft preparation, M.B., W.M.D. and M.K.H.; writing review and editing, M.B., W.M.D. and M.K.H. All authors have read and agreed to the published version of the manuscript.

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