Silver nanoparticles (AgNPs) as photocatalyst in the photodegradation of rhemazol brilliant blue

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Abstract. The phytosynthesis of silver nanoparticles (AgNPs) and its use as a photocatalyst to photodegrade rhemazol brilliant blue are discussed. The AgNPs was prepared by reducing Ag+ from 0.01 M AgNO3 using frangipani (Plumeria rubra) water extract. The photodegradation was conducted by irradiating the suspension of the coloring agent and the AgNPs with UV rays at 259 nm. The optimum pH, AgNPs volume, and irradiation time were determined by measuring the degradation percentages at various pH, AgNPs volumes, and irradiation times. The study found that the optimum photodegradation occurred at pH 4, using 10 mL AgNPs, and irradiated for 60 minutes. Under the optimum conditions, AgNPs is capable of effectively photodegrading (97.84 ± 1.09) % of 600 ppm rhemazol brilliant blue.

1. Introduction
Among the known nanomaterials, silver nanoparticle (AgNPs) is getting a lot of attention because of their non-toxic nature and various benefits, including as antibacterial agents for various types of microorganisms that cause various types of diseases [1]. Apart from its use in biology, AgNPs has the potential to be applied in various fields, including as an optical sensor and as a photocatalyst [2]. Its photocatalytic activity in the photodegradation of dyes has been reported in several studies. Vanaja et al. [3] reported that 95% of methylene blue dye can be degraded within 72 hours. Saeed et al. [4] successfully degraded 90% of methylene orange dye within 6 hours, at pH 2, using a photocatalyst from polyacrylonitrile nanofiber modified AgNPs. AgNPs can also degrade 98.3% of the dye methylene purple 6B for 4 hours and the methylene orange dye in 1 hour [5]. Research conducted by Kulkarni & Bhanage [6] showed that Ag nanoparticles (AgNPs) from sugar cane juice were able to degrade all samples of methyl orange dye in 21 minutes and degrade almost all samples of methylene blue dye within 50 minutes. Jyoti & Singh [7] synthesized AgNPs from Zanthoxylum armatum leaves which can degrade several dyes very quickly and efficiently.

Silver nanoparticles can be made by physical or chemical methods, which have their respective weaknesses. The former is expensive and difficult [8], while the latter causes toxic effects due to the hazardous materials used. A relatively new method that can be used to synthesize a catalyst into nanoparticle size is a reduction of metal ions using metabolites from plants, referred to as biosynthesis [9] or phytosynthesis [6]. This method can produce nanoparticles that are safe and environmentally
friendly (Green synthesis) because it can minimize the use of harmful inorganic materials. This synthesis method is very effective because it is fast, non-toxic and environmentally friendly technology [10]. In principle, AgNPs biosynthesis is reducing Ag$^+$ to Ag in an autocatalytic reaction by secondary metabolites such as terpenoids, flavonoids, alkaloids, quaternary isoquinoline alkaloids, aporphyrine alkaloids etc. In several studies, these compounds are able to produce or form nanoparticles from a metal [10, 11].

In this study, AgNPs was synthesized using a water extract of frangipani flower (Plumeria rubra) which is very abundant in Bali. This flower water extract contains bioactive compounds such as tannins, phenols and vitamin C [12]. The AgNPs produced is used as a photocatalyst to degrade the brilliant blue Rhemazol dye which is widely used in the textile dyeing industry in Bali.

2. Experimental section

2.1. Materials
The materials used in this study included Plumeria rubra powder, Rhemazol brilliant blue dye, AgNO$_3$ (Sigma-Aldricht), demineralized water, and distilled water.

2.2. Apparatus
Equipment used apart from the usual laboratory glass wares and equipment, were black plastic sheets, irradiation boxes with a UV lamp (Philips TUV 15 W/G15 T8). The instruments were UV-Vis spectrophotometer (Shimadzu 2600) and Particle size analyzer (PSA from Malvern).

2.3. Procedure
Twenty grams of dry Plumeria rubra powder was added into 100 mL demineralized water and heated at 60°C for 15 minutes. The mixture was then left to stand for 24 hours, and filtered. The filtrate was then mixed with 0.01 M AgNO$_3$ solution (1:10 v/v) and heated at 60°C for 20 minutes. The AgNPs produced was characterized by measuring its absorbance in the range of 400-500 nm [13] and by measuring its particle size using PSA.

The optimum volume of the photocatalyst was determined by varying the volume of the catalyst by 5, 10, 15, 20, and 25 mL in 25 mL of 50 ppm aqueous dye solution. The optimum pH was determined by irradiating the25 mL of 50 ppm of dye solution at pH 2, 4, 6, 8, and 10. The optimum irradiation time was determined by irradiating 25 mL of 50 ppm of dye solution with UV light at the optimum pH, the optimum amount of catalyst for 30, 60, 90, 120, 150, and 180 minutes.

Photodegradation capacity was studied by irradiating 25 mL of 50, 100, 200, 300, 400, 500, and 600 ppm rhemazol brilliant blue under the optimum conditions. The percentage of degradation was obtained using the equation:

\[ D \, (\%) = \frac{C_0 - C_t}{C_0} \times 100\%. \quad (1) \]

3. Results and discussion

3.1. The characteristics of the AgNPs
The growth of AgNPs can easily be observed using UV-Vis absorption. Qualitative analysis of AgNPs growth can be carried out based on the specific characteristics of the Surface Plasmon Resonance (SPR) of the nanoparticles. SPR is a collection of oscillations against electron conduction that occurs on the surface of the material. The presence of an electromagnetic field generated by electromagnetic waves causes the excitation of the oscillatory collection of electrons in metal nanoparticles, which is called Localized Surface Plasmon Resonance [14]. The change in color from yellow to reddish brown indicates the formation of silver nanoparticles as a result of the SPR phenomenon. The UV-Vis spectra of the silver particles produced is shown in figure 1. The spectra show that the particles, having maximum absorbance between 400 and 500 nm, can be categorized as nanoparticles [13]. The spectra also indicate that the AgNPs is stable for at least 29 hours to stand at room temperature. This stability is an advantage for users
in case there is a delay in the application of the AgNPs. Figure 2 shows the result of the particle size distribution analysis. It shows that the silver particles produced in this research have a very good size uniformity at 18.98 nm. This confirms that the silver particles produced fulfil the nanoparticle category. More importantly, the AgNPs can be used as photocatalyst for the degradation of pollutant molecules such as Rhemazol brilliant blue.

**Figure 1.** UV-Vis spectra of AgNPs after 1, 4, 6, 29, and 53 hours aging.

**Figure 2.** The size distribution of the AgNPs.

### 3.2. The Optimum volume of photocatalyst
Since the AgNPs present as a suspension, the amount of the photocatalyst used in the photodegradation is measured as volume. This study reveals that to photodegrade 25 mL of 50 mg/L Rhemazol brilliant blue we only need 10 mL of the AgNPs suspension, which is about 0.1 mmol AgNO₃. Figure 3 shows the degradation percentages change with the volume of the AgNPs suspension. It is clearly shown that using more than 10 mL AgNPs decrease the percentage of the degradation. It is apparently due to reducing clarity of the mixture which prohibits light reaching the dye molecules. As a consequence, further photodegradation cannot be achieved.

### 3.3. Optimum pH for the photodegradation
Figure 4 shows that the optimum photodegradation occurs at pH 4. Upon UV irradiation, the silver atoms excite their 4d electrons to 5sp leaving holes in the valence band [15]. The excitation is enhanced under the acidic condition, making its surface positively charged. Since Rhemazol brilliant blue is an anionic molecule, it easily gets in contact with the photocatalyst. In the same instance, the electron holes react with H₂O to
form hydroxyl radicals (OH•) which can degrade the dye. The electrons excited readily react with oxygen to produce more radicals (O₂•) which also degrade the dye molecules. Degradation percentage tends to decrease with increasing pH. The percentage decrease in alkaline degradation may be due to the alkaline OH\(^-\), which, although can form hydroxyl radicals, the excessive number of the OH react with hydroxyl radicals (OH•) or the hydroxyl radical recombine into new compounds [16, 17]. Moreover, the optimum pH is also beneficial for the photodegradation procedure of Rhemazol brilliant blue, since the pH is actually the original pH of an aqueous solution of the dye agent; thus no additional acid or base would be required for adjusting the system to achieve the optimum pH.

![Figure 3](image1.png)

**Figure 3.** The photodegradation percentages at various photocatalyst volumes.

![Figure 4](image2.png)

**Figure 4.** The change of photodegradation percentage with pH.

3.4. *Optimum irradiation time*

From figure 5 it can be seen the effect of irradiation time on the percentage of degradation, where the percentage of degradation increases to up to 99% within 60 minutes irradiation. The percentage decreases with longer irradiation time than 60 minutes, although the figure is still higher than 90%, which is very good. This means that the photocatalytic activity has reached its maximum at 60 minutes, which is very effective, much faster than that using other catalysts such as metal oxide-clay composites [18].

3.5. *The effectiveness of photodegradation of rhemazol brilliant blue*

The photodegradation capacity was investigated by irradiating aqueous dye solution with a varied. This is confirmed by the fact that irradiation process without AgNPs can only reduce the concentration of the dye by less than 50%. If this procedure is applied to liquid waste containing dye agents, it will leave less than 10 ppm dye if the initial concentration is as high as 600 ppm which is unlikely. Therefore, this
AgNPs is an effective photocatalyst for the photodegradation of rhemazol brilliant blue. In our previous work this AgNPs was also effective as a photocatalyst for degrading indigosol blue [19,20] and methylene blue. Indigosol blue and Rhemazol brilliant blue are anionic dye, while methylene blue is cationic, thus it may suggest that photodegradation using AgNPs catalyst is an effective method to remove dye pollutant from liquid waste.

![Figure 5. The change in degradation percentage with irradiation time.](image)

**Table 1.** The degradation percentages of rhemazol brilliant blue by UV light with and without AgNPs.

| Initial dye concentration (ppm) | Degradation percentage (%) |
|--------------------------------|-----------------------------|
| 50                            | 44.68 ± 1.05                |
| 100                           | 99.77 ± 1.21                |
| 200                           | 99.69 ± 1.18                |
| 300                           | 99.45 ± 1.19                |
| 400                           | 99.22 ± 1.16                |
| 500                           | 98.67 ± 1.11                |
| 600                           | 97.84 ± 1.09                |

*without AgNPs

4. **Conclusion**
The AgNPs is proven to have the photocatalytic capability in degrading rhemazol brilliant blue molecules. Under pH 4, 10 mL of the AgNPs suspension effectively removes 97.84 ± 1.09 % of 25 mL of 600 ppm Rhemazol brilliant blue during 60-minute UV irradiation. This result proves that AgNPs can be used as a photocatalyst with high capacity to photodegrade rhemazol brilliant blue, and potentially capable of treating waste containing dye agents.

5. **Suggestion for future work**
AgNPs theoretically works with visible light, which is preferable to UV. Future research should study the photocatalytic activity of the AgNPs using visible light or sunlight.

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