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Utilization of Silver Nanoparticles as Adsorbent of Methylene Blue

Nindita Clourisa Amaris Susanto[1]*, Nadiatul Fajri[2], Yoga Pratama[2], M. Reza Prasetio[2], Rahayu[3], Aulia Ratri Hapsari[4]

[1]Vocational School, Universitas Sebelas Maret, Surakarta, Indonesia
[2]Department of Chemistry, Faculty of Science and Technology, Universitas Jambi, Jambi, Indonesia
[3]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Pattimura, Ambon, Indonesia
[4]School of Chemistry, University of Birmingham, United Kingdom

*Corresponding author: nindita_clourisa@staff.uns.ac.id

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Abstract

This study has successfully synthesized silver nanoparticles (Ag NPs) using banana stem extract as the bioreductor and reported its application in adsorption of methylene blue (MB). Adsorption of MB was tested under ultraviolet light by varying pH solution values (3, 4, 5, 7, 9, 10, and 11), irradiation times (0,5, 1, 2, 3, 4, 5 hours), and MB concentrations (50, 100, 150, and 200 ppm) to determine their optimum values. The results revealed that the optimum pH value and irradiation time were at 9 and 1 hour, demonstrating the highest deconcentration percentage (%D) of 89.19% and 94.58%, respectively. The %D of MB dye by samples with concentrations of 50, 100, 150, and 200 ppm were 86.294%, 78.416%, 69.366%, and 66.638%, respectively, with an average of %D of 75.189%. The least degraded MB was 90.643 mg, obtained at 50 ppm. Meanwhile, the most degraded MB was 280.181 mg, attained at 200 ppm. The average concentration of degraded MB was 188.538 mg/gr.

Keywords: *silver nanoparticles; adsorption; methylene blue*

Introduction

Silver nanoparticle (Ag NPs) synthesis can be done by using plant extracts as a bio-reductor to reduce Ag^+ species to Ag^0 (Chen et al., 2019; Rahma & Suratno, 2023; Sharifi-Rad et al., 2023). Extract of plabt acts as reducing and natural capping agents for the reductin in silver ion and stabilization of silber nanoparticles (Singh et al., 2013; Momeni et al., 2017).This process involves secondary metabolite compounds from plants, such as terpenoids, ketones, aldehydes, amides, and carboxylates (Shankar et al., 2004). Bioreductors can be obtained from natural materials containing antioxidant compounds or polyols that can reduce silver (Arifin, 2016; Karan et al., 2024) and functional groups that can play a role in reducing silver ions into Ag nanoparticles, including hydroxyl (-OH) and amine (-NH) groups (Masakke et al., 2015; Mechouche et al., 2022). Banana plant stems comprise complex secondary metabolite compounds. Phytochemical screening results show the presence of saponins, triterpenoids, steroids, flavonoids, tannins, and quinones in Banana plant stems (Komala et al., 2018). Therefore, banana plant stems can have the potential as a bioreductor.

Adsorption is a method widely employed in liquid waste treatment. The materials used to process waste are expected to be cheap and Exeasy to obtain (Taba et al., 2019). Methylene Blue (MB) is a vital basic dye and is relatively inexpensive compared to other dyes. This dye is often used in the textile, silk, wool, and cosmetics industries. This dye waste is extremely harmful if it is thrown into the waters. Therefore, adsorption is required to treat this waste to become less toxic. Several previous studies on the adsorption of MB using Ag NPs (Marimuthu et al., 2020; Gowda et al., 2022;). Synthesized Ag NPs with basil leaf extract bioreductor obtained an absorption capacity of 77.90% with a particle size of 70.19 ± 0.89 (Bere et al., 2019). Besides, other research also exploited water hyacinth as a Ag NPs bioreductor, obtaining an absorption capacity of 49.3% due to the non-uniform particle size (Kasim et al., 2020). According to the background, this study reported the synthesis of Ag NPs using banana stem extract bioreductor where Ag NPs were applied as MB deconcentration.

Methods

Tools and materials

The tools employed in this research were analytical scales, tissue, a cutter, a set of standard glassware (Pyrex brand), a spatula, stirring rod, dropper pipette, Whatman No. 1 filter paper, mortal pestle, magnetic stirrer, oven, Whatman No. 1 paper, centrifuge, and pH meter. The instruments for the characterization were UV-VIS spectrophotometer (Biochrom brand), Scanning Electron Microscopy (SEM) (Brand FEI), Particle Size Analyzer (PSA). Meanwhile, the material used in this research included banana stem extract, $AgNO_3$, MB, HCl, and NaOH.

Procedures

Nanoparticle Synthesis

First, 100 mL of banana stem extract was mixed into 40 mL of 0.05 M $AgNO_3$ solution by stirring with a magnetic stirrer for 24 hours until a precipitate formed (Fajri et al., 2022). Then, the mixture was centrifuged at 3500 rpm for 10 minutes, resulting in filtrate and residue. The residue was dried in an oven at 100^{o}C for 2 hours. The dry sediment was then crushed to obtain powder silver nanoparticles and weighed. The Ag NPs characterizatin was perfomed using UV-Vis spectrophotometer, SEM and PSA. The stability testing was carried out by measuring the surface plasmon resonance (SPR) used a UV-Vis spekctrophotometer for 5 days.

Determination of Optimum pH

Five of the 100 mL Erlemyer flasks were filled with 50 mL of 50 ppm MB and a number of Ag nanoparticles. The pH of the mixture was adjusted to values of 3, 4, 5, 7, 9, 10, and 11 by adding 0.01 M HCl solution for the acid pH and 0.5 M NaOH for basic pH, measured with a pH meter. Each suspension was irradiated with ultraviolet light for 30 minutes while stirred with a magnetic stirrer. After irradiation, the irradiated suspension was filtered, and the absorbance was measured using a UV-VIS spectrophotometer at a wavelength of 664 nm (Bere et al., 2019). The optimum pH was chosen from the sample showing the best percentage deconcentration of MB.

Determination of Optimum Irradiation Time

Five of the 100 mL Erlenmeyer flasks were filled with 50 mL of 75 ppm MB and a number of Ag nanoparticles and set at the optimum pH. Each suspension was irradiated with UV light for 1 to 5 hours in a 1-hour interval while stirred with a magnetic stirrer. After irradiation, the suspension was filtered, and the absorbance was measured using a UV-VIS spectrophotometer at a wavelength of 664 nm (Bere et al., 2019). The optimum irradiation time was chosen from the sample, demonstrating the best percentage deconcentration of MB.

Adsorption of MB

Four of the 100 mL Erlemeyer flasks were filled with 50 mL of MB with various concentrations from 50 to 200 ppm in 50 ppm intervals. They were mixed with a number of Ag nanoparticles and set at the optimum pH. Each suspension was irradiated with UV light for the optimum time while stirred with a magnetic stirrer. The absorbance of the irradiated suspension was measured with a UV-VIS spectrophotometer at a wavelength of 664 nm (Bere et al., 2019).

Result and Discussion

Synthesis of Ag NPs

Synthesized Ag NPs using biological materials in plants, banana stems, as the bioreductor was successfull. The formation of nanoparticles can be physically observed as indicated by the observed color changes (Safaepour et al., 2009). Ag NPs show a brown color change in solution due to plasmon excitation on the surface of the Ag NPs. The color change shown in Figure 1 is due to the reduction of silver ions, indicating the formation of Ag NPs (Gavhane et al., 2012). The more bioreductant in the banana stem extract can induce the more Ag^{+} ions reduced so that the color of the Ag NPs formed becomes more intense (Sari et al., 2017).

UV-Vis analysis was further conducted on the filtrate to identify the presence of Ag Nanoparticles, revealed at a maximum wavelength of 440 nm. This light is visible and can be seen by the human eye. Absorption of visible light causes electrons to be excited. The UV-Vis spectra for Ag nanoparticles are shown in Figure 2.

Figure 1. Ag NPs Solution

Salasa et al. (2016) demonstrated that UV-Vis spectrophotometer measurements were performed to obtain the characterization of Ag NPs based on their absorbance peaks, showing that silver ions have been reduced to Ag. It is demonstrated by the formation of silver nanoparticles characterized by the maximum wavelength at 400-450 nm (Rajkumar et al., 2021).

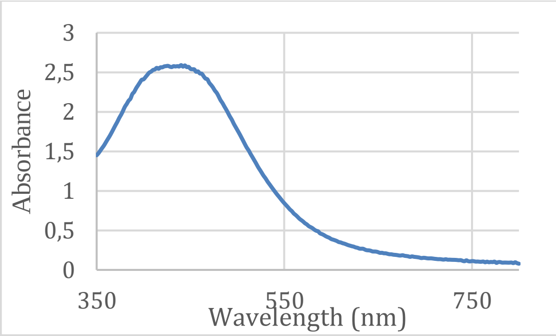

Figure 2. UV-Vis Spectrophotometer spectra of Ag nanoparticles

The stability of Ag NPs was measured using spetrophotometer UV-Vis for 5 days. The measurement data are shown in Table 1. Measurements from days 1 to 5 provide wavelength with a range 438-444 nm. This wavelength is still within the SPR characteristic range of Ag NPs. It means stable for 5 times observation. Wavelength maximum measurement oer 5 times shown in Figure 3.

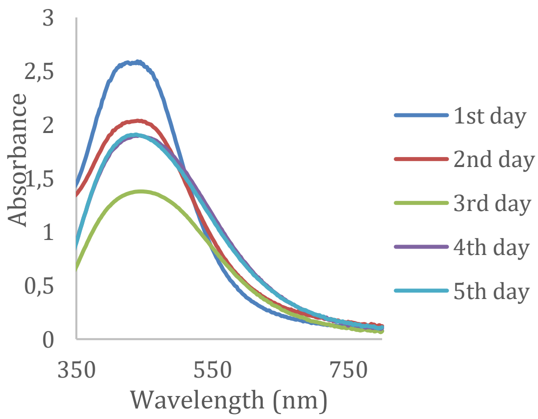

Figure 3. UV-Vis Spectra on Ag NPs Stability

The colloid obtained was analyzed using SEM with 5000x magnification to determine the morphology of Ag nanoparticles. The SEM

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image (Figure 3) shows that the silver nanoparticles are slightly spherical and have uneven surfaces. Distribution of particles was measured using PSA, and the result Ag NPs have average diameters 97,5 nm.

Table 1. Ag NPs data measurements

Ag NPs	λmax (nm)	Absorbance
1st day	440	2,59067
2nd day	440	2,03769
3rd day	444	1,37735
4th day	442	1,89874
5th day	438	1,90835

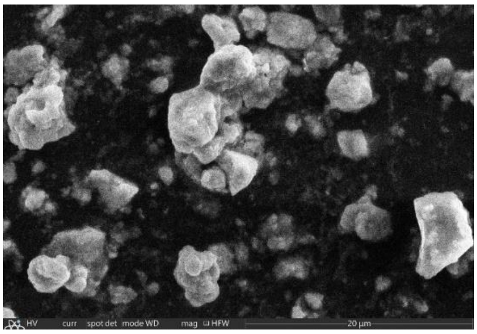

Figure 3. The SEM image of Ag NPs with 5000x magnification

Adsorption of MB

The use of silver nanoparticles as a deconcentration of MB was performed by optimizing the pH and irradiation time parameters. The optimum pH was determined by adjusting the pH conditions at 3, 4, 5, 7, 9, 10, and 11 values and found the highest deconcentration percentage (%D). Figure 4 presents %D of MB as the function of pH values of solutions. It reveals that the optimum value was obtained at pH 9, showing the highest %D of 89.192%. It means the optimum pH condition to achieve the MB deconcentration is in an alkaline environment. This result is in line with the research results of Huda *et al.* (2018), exhibiting that the optimum pH was attained at about 9.

The optimum irradiation time for MB deconcentration was obtained at 1 hour with %D = 94.581%, as shown in Figure 5. In another research (Sari et al., 2017; Benhachem et al., 2019), the optimum time value was also obtained at 1 hour, where the time was effective and the percentage degradation value was very high.

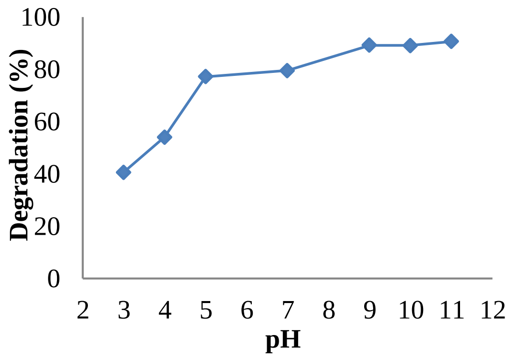

Figure 4. Correlation curve of % Degradation of MB with solution pH values

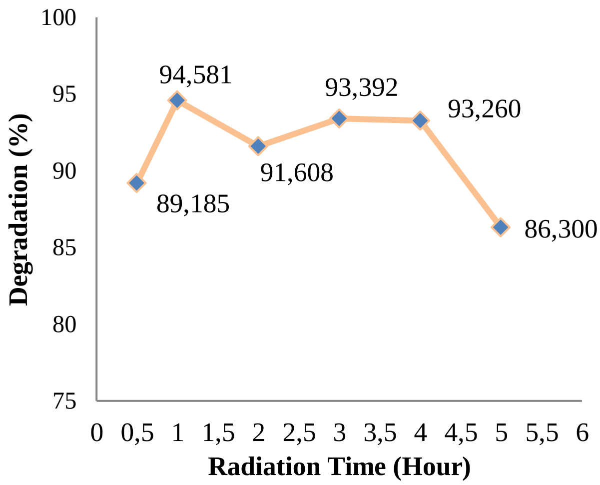

Figure 5. % Degradation of MB dye vs irradiation times

Table 2. Results of the adsorption of MB

Irradiation Time (Hours)	Initial MB Concentration (mg/L)	MB Adsorption Capacity (mg/ gr)	%D
1	50	90.643	86.29
1	100	164.739	78.41
1	150	218.590	69.36
1	200	280.181	66.68
Average		**188.538**	**75.18**

Adsorption of MB is expressed as %degradation. Table 2 presents the results of MB deconcentration using Ag nanoparticles synthesized using banana stem extract as the bioreductor. Based on the %D values, the effectiveness of silver nanoparticles in degrading MB is classified as good, where the average %D value is 75.18% with an average adsorption capacity of 188.538 mg/g.

Conclusion

Adsorption of MB has been successfully performed using silver nanoparticles synthesized using banana stem extract bioreductor. Based on the results, maximum MB adsorption has been achieved at optimum parameters of pH 9 and irradiation time of 1 hour. The average value of % MB degradation was 75.18%, with an average adsorption capacity of 188.538%.

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