Jurnal Akta Kimia Indonesia

INDONESIA CHIMICA ACTA

PAPER

View Article Online
View Journal View Issue

Cite this: *Indo. Chim. Acta.*, 2023, **16**, **2**.

Received Date:
19th August, 2023
Accepted Date:
16th October, 2023

Keywords:
Bioreducer;
Photodegradation;
Methylene blue;
Silver nanoparticles;
Tagetes erecta;

DOI:
http://dx.doi.org/10.20956/ica.v16i2.28376

Synthesis of Silver Nanoparticles Using Marigold (*Tagetes erecta*) Flower Extract for Photodegradation of Methylene Blue Dye

Iryanti Eka Suprihatin[1*], Najwa Kusuma Putri Antariksa[1], I Gusti Ayu Kunti Sri Panca Dewi[1], Gusti Ayu Dewi Lestari[2], and Pande Made Intan Wahyuni[1]

Abstract. The utilization of methylene blue dye in the textile industry can have a significant environmental impact due to its high toxicity. To address this issue, a study was conducted on the photodegradation of methylene blue dye using silver nanoparticles (AgNP) synthesized with marigold (*Tagetes erecta*) flower extract as a bioreducer. This article reports on the synthesis of AgNP and its application in the photodegradation of methylene blue dye. The synthesis of AgNP involved the reduction of $AgNO_3$ with marigold flower extract. Different ratios of marigold flower extract to $AgNO_3$ solution (0.01 M) were used: 1:9, 2:8, 3:7, 4:6, and 5:5. The formation of AgNP was monitored at various time intervals using UV-Vis spectroscopy. The best AgNP sample was measured using a Particle Size Analyzer (PSA). The research results indicated that the optimal condition was achieved at a marigold extract to $AgNO_3$ ratio of 2:8, with the UV-Vis spectrum showing a peak at a wavelength of 411 nm. The optimum conditions for photodegradation were as follows: AgNP volume of 15 mL, irradiation for 30 minutes, and pH 4. Under these conditions, photodegradation of methylene blue dye achieved a reduction of up to 72.46% from the initial concentration of 100 ppm.

Introduction

The rapid development of the textile industry in Indonesia has led to a significant increase in the generation of wastewater containing various synthetic dyes that are difficult to degrade. Normally, these dye waste substances can naturally decompose under sunlight; however, the limited intensity of UV light reaching the water bodies results in a slow dye decomposition reaction. As a result, the accumulation of dyes at the bottom of water bodies or soil occurs more rapidly than their photodegradation process (Dae-Hee *et al.*, 1999; and Alkadasi, 2004). One of the dyes that is challenging to natural degradation or decomposition is methylene blue (MB}.

Methylene blue is commonly used for dyeing cotton, wool, silk, leather, and paper coatings due to its vibrant color properties, which facilitate quick and easy dyeing processes (Choi & Yu, 2019; Nurhasni & Hendrawati, 2018). In the dyeing process, around 5% of the MB compound is utilized, while the remaining 95% is discarded as waste. The presence of this dye significantly impacts the environment due to its high toxic effects, which can cause skin allergies, irritation, genetic changes, and carcinogenicity (Salazar-Rabago *et al.*, 2017).

To address this issue, numerous studies are currently being conducted to enhance the performance of wastewater treatment applications through photocatalysis. One approach that has been explored is the photodegradation of dyes using silver nanoparticle (AgNP) photocatalyst synthesized using extracts from basil and frangipani plants (Lestari *et al.*, 2019; Suprihatin *et al.*, 2020) as bioreductor.

Silver nanoparticles (AgNP) are silver particles with sizes ranging from 1 to 100 nm. This small size influences the properties of these metal nanoparticles. According to Susmanto *et al.*, (2020), smaller particle sizes result in

[1]*Chemistry Study Program, Faculty of Mathematics, and Natural Sciences, Udayana University, Badung, Indonesia;* ***Email: eka_suprihatin@unud.ac.id***
[2] *Mahaganesa School of Pharmacy, Denpasar, Indonesia.*

larger surface areas, leading to a greater number of active sites and, consequently, faster reaction processes. Several studies have demonstrated that silver nanoparticles can act as photocatalysts for dye degradation. Lestari *et al.*, (2019) reported a 94.75% degradation of indigosol blue dye using AgNP after 4 hours of irradiation, and Suprihatin *et al.*, (2020) showed that silver nanoparticles can degrade around 97% of 600 ppm Remazol brilliant blue dye with 60 minutes of irradiation. Additionally, Zare-Bidaki *et al.*, (2022) demonstrated that AgNP can degrade 94.37% of thymol blue and 90.12% of malachite green dyes within 100 minutes of irradiation.

This article presents the results of a study on the synthesis of AgNP using extracts from marigold flowers (*Tagetes erecta*) and its application as a photocatalyst for the photodegradation of methylene blue dye. Marigold has been reported to contain bioactive compounds having antioxidant activities including flavonoids, triterpenoids, polyphenols, quercetin, and quercetagetin (Gong, *et al*, 2012; Huang *et al*, 2022). These antioxidant contents put the marigold amongst the plants whose flower extract can reduce metal ions such as Ag^+ to their atoms. This study shows that water extract of the flower has successfully assisted in sinthezising AgNP.

Experimental

Material and Methods

The materials used in this study included *Tagetes erecta* flowers, deionized water (Demineralized water), methylene blue dye, magnesium powder (Mg), concentrated hydrochloric acid (HCl), ferric chloride ($FeCl_3$) 5%, chloroform (CH_3Cl), acetic anhydride ($(CH_3CO)_2O$), concentrated sulfuric acid (H_2SO_4), 2N HCl, Dragendorff reagent, Mayer reagent, silver nitrate ($AgNO_3$) 0.01 M, 0.1N HCl, 0.1N sodium hydroxide (NaOH), and filter paper.

The equipment used included a blender, 100 mL beakers, measuring cylinders, reaction tubes, droppers, volumetric pipettes, analytical balance, magnetic stirrer, black plastic wrap, radiation box, oven, and UV lamp at 259 nm. The testing instruments included the Shimadzu UV-VIS 1800 spectrophotometer and Malvern MS300 particle size analyzer.

Procedures

Preparation of Marigold Flower Aqueous Extract

Fresh marigold flowers (*Tagetes erecta*) weighing 2.5 kg were cleaned with tap water, rinsed with demineralized water, and dried. The dried flowers were powdered using a blender and stored in a closed container. 15 grams of flower powder were mixed with 300 mL of demineralized water in a 1000 mL beaker and heated at 60°C for 15 minutes. The mixture was left to stand for 24 hours and then filtered using Whatman filter paper. The obtained extract was stored in a refrigerator if not used immediately (Suprihatin, 2020).

Phytochemical Screening

Flavonoid Test. 2 mL of extract was mixed with 3 mL of hot water, boiled for 5 minutes, filtered, and the filtrate was treated with 0.05 mg of magnesium powder and 1 mL of concentrated HCl. Positive results were indicated by the formation of red, yellow, or orange color (Harborne, 1987).

Phenol Test. 2 mL of extract was mixed with 2 drops of 5% $FeCl_3$ solution. Positive results were indicated by the formation of green or bluish-green color.

Synthesis and Characterization of Silver Nanoparticles

Aqueous extract of marigold flowers (*Tagetes erecta*) was mixed with 0.01 M AgNO3 solution in various ratios: 1:9, 2:8, 3:7, 4:6, and 5:5. The mixture was heated at 60°C for 20 minutes. Nanoparticle formation was observed at different time intervals (2, 4, 6, 29, and 49 hours) using UV-Vis spectrophotometer. Particles showing the sharpest absorbance between 400 and 500 nm were characterized using Particle Size Analyzer (PSA).

Photocatalytic Activity Optimization of AgNP Volume

Five 100-mL beakers wrapped in black plastic were each filled with 25 mL of 50 ppm MB solution. Different volumes (1, 2, 5, 10, 15, and 20 mL) of AgNP were added to each beaker. The beakers were placed in a radiation box, and the plastic wrap was removed. The mixtures were irradiated with UV light and stirred with a magnetic stirrer for 1 hour. After irradiation, the mixtures were centrifuged, and the absorbance of the supernatant was measured at 664 nm using a UV-Vis spectrophotometer. The percentage of degradation was obtained using the equation (1):

$$D\ (\%) = \frac{(Co - Ct)}{Co} \times 100\% \qquad (1)$$

Optimization of Irradiation Time

Similar to the previous step, 25 mL of 50 ppm MB solution was placed in five beakers with the optimum AgNP volume. The mixtures were irradiated for different time intervals (10, 20, 30, 60, and 90 minutes) with UV light and stirred with a magnetic stirrer. Absorbance measurements and calculations similar to the previous step were performed.

Optimization of pH

Five beakers with 25 mL of 50 ppm MB solution and the optimum AgNP volume were prepared. The pH of the mixtures was adjusted to pH 2, 4, 6, 8, and 10 using 0.1 N HCl or 0.1 N NaOH. The mixtures were irradiated and stirred, and absorbance measurements were taken.

Determination of Photodegradation Effectiveness

The effectiveness of MB photodegradation was determined by measuring the percentage degradation of MB solutions with different concentrations under optimum conditions. Beakers with a 100 mL capacity wrapped in black plastic were filled with 25 mL of MB solutions at concentrations of 100, 200, 300, 400, 500, 600, and 700 ppm. Optimum AgNP volume and pH were added to each beaker. The mixtures were irradiated, stirred, and absorbance measurements were performed. The percentage degradation was calculated using Equation (1).

Result and Discussion

Phytochemical Screening

This preliminary test was conducted to determine the presence of flavonoids and phenols in the extract of marigold flowers (*Tagetes erecta*). The test results indicated that the marigold flower extract contains both groups of compounds. Therefore, this extract can be used as a bioreducer in the synthesis of silver nanoparticles.

Synthesis and Characterization of Nanoparticles

Silver nanoparticles with volume ratios of 1:9, 2:8, 3:7, 4:6, and 5:5 appeared dark brown during the synthesis process, indicating the formation of nanoparticles (Zielinska *et al.*, 2009). To confirm this indication, analysis was performed using UV-Vis spectroscopy. Based on the analysis results obtained using UV-Vis spectroscopy, particles from the 1:9 and 2:8 volume ratios met the characteristic criteria of AgNP, with the sharpest absorbance occurring at wavelengths between 400-500 nm. In the 1:9 ratio, AgNP exhibited an absorption peak at 413 nm for storage times of 2-29 hours, while in the 2:8 ratio, an absorption peak was observed at 411 nm for storage times of 2-6 hours. Other ratios did not exhibit an intense peak within the 400 and 500 nm range. Furthermore, the quantity of nanoparticles formed can be determined from the absorbance values (Haryani *et al.*, 2016). Among the volume ratio variations, the 2:8 ratio had the highest absorbance value, specifically at a storage time of 4 hours, indicating the formation of a significant amount of silver nanoparticles. UV-Vis spectra showing the development of silver nanoparticles over time are displayed in Figures 1 and 2.

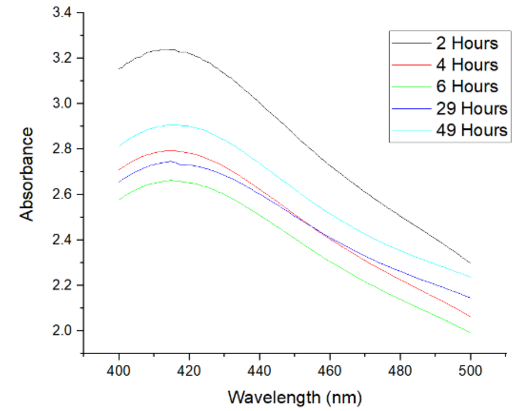

Figure 1. UV-VIS spectrum of AgNP in the 1:9 ratio.

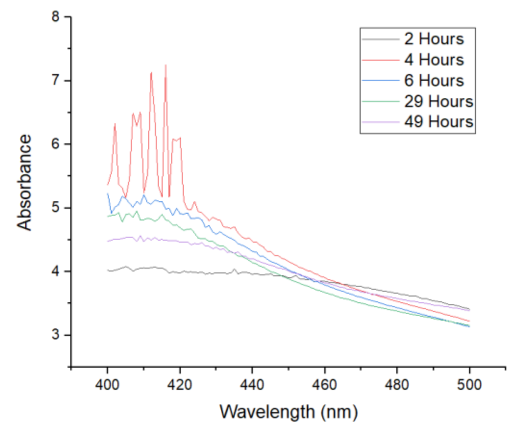

Figure 2. UV-VIS spectrum of AgNP in the 2:8 ratio.

The AgNP samples obtained from two different volume ratios, specifically the 1:9 and 2:8 ratios, exhibited peaks within the wavelength range of 400-500 nm. These samples were subjected to Particle Size Analysis (PSA) for further examination. According to the measurements obtained from the Particle Size Analyzer (PSA), the size of the silver nanoparticles (AgNP) generated at a ratio of 1:9 was 252.6 nm, exhibiting a uniformity of 96.6%. In contrast, the AgNP synthesized at a ratio of 2:8 had a size of 153.9 nm with a uniformity of 100%. Based on the provided data, it can be observed that the utilization of a 2:8 ratio resulted in the production of smaller AgNP particles. Consequently, this particular volume ratio is thought to be better for making the photocatalyst in the process of degrading methylene blue with light. The obtained particle size does not necessarily mean that the particles are not nanoparticles for two reasons: first, the UV-VIS spectrum already shows that nanoparticles are present, and second, AgNP can clump together because it takes 14 days between making the particles and analysing them with PSA. For application as a photocatalyst, fresh AgNP was synthesized with a 2:8 ratio to prevent agglomeration.

Photocatalytic Activity Optimization of AgNP Volume

The photodegradation results of methylene blue with varying AgNP volumes are shown in Figure 3. Up to 15 mL of AgNP, the percentage of degradation of methylene blue steadily increased with the increasing volume of nanoparticles used, and then levelled off. Therefore, the effective optimum value was found by picking the level of photodegradation with the least amount of silver nanoparticles, which was 84.59% with a volume of 15 mL.

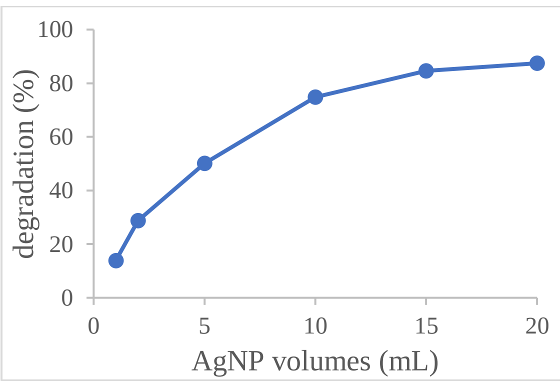

Figure 3. Influence of AgNP volume on the degradation of 50 ppm methylene blue.

Optimization of Irradiation Time

As shown in Figure 4, during the initial irradiation period (10-20 minutes), the AgNP catalyst did not exhibit a significant response to the photodegradation of methylene blue. However, after irradiation time reached 30 minutes, the AgNP catalyst displayed a substantial increase in activity, leading to a sharp increase in the percentage of photodegradation from 76.09% to 82.24%. This improvement occurs as the duration of degradation increases, allowing for more contact between the catalyst and the dye molecules, thereby enhancing the photodegradation process. This increase is attributed to the cumulative effect of UV radiation, resulting in more photons interacting with silver nanoparticles, leading to increased formation of hydroxyl radicals (OH●) (Bere *et al.*, 2019). However, after 30 minutes of irradiation, the photocatalyst's ability to degrade gradually decreases to 80.13% after 90 minutes. Therefore, the optimal irradiation time is determined to be 30 minutes, achieving a photodegradation percentage of 82.24%.

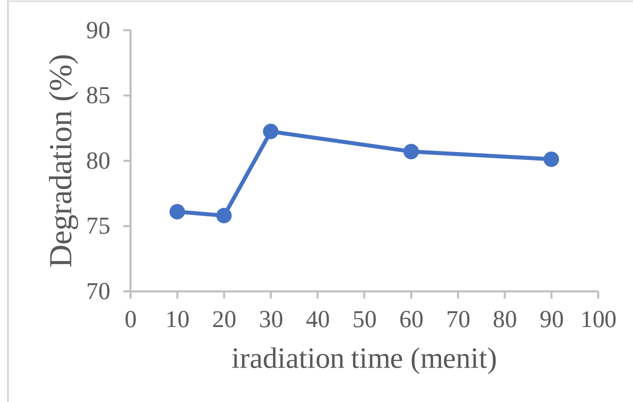

Figure 4. Influence of irradiation time on the degradation of 50 ppm methylene blue.

Optimization of pH

From Figure 5, it is evident that the degradation percentage increases from pH 2 to pH 4, with the highest degradation percentage observed at pH 4 (84.58%). However, after pH 4, the photocatalyst's degradation ability decreases. At pH 2, which is very acidic, less methylene blue is broken down than at pH 4. This is because the surface of the AgNP photocatalyst is saturated with H+ ions, which gives it a positive charge. Methylene blue, being positively charged, has difficulty adsorbing onto the positively charged surface of the silver nanoparticles due to strong repulsive forces between them. On the other hand, when the pH is higher than 4, the amount of degradation goes down because the surface charge of the nanoparticle becomes more negative. This makes positively charged methylene blue molecules stick to AgNP very strongly. Because of this, methylene blue molecules cover the surface of the photocatalyst, which makes it less able to absorb radiation (Suprihatin *et al.*, 2022).

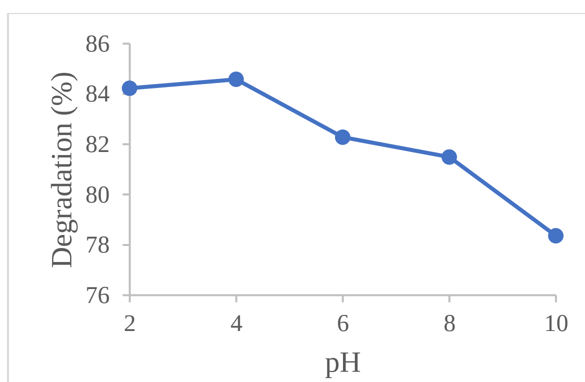

Figure 5. Influence of pH on the degradation of 50 ppm methylene blue

Photodegradation Effectiveness

Determining effectiveness aims to demonstrate that the method used is effective in degrading methylene blue dye.

Table 1. Degradation results of various methylene blue initial concentrations

Intial [MB] (ppm)	Degradation percentage (%)
50	84,58
100	72,46
200	55,66
300	42,88
400	41,90
500	33,69
600	30,25
700	31,13

Conclusion

This study shows that *Tagetes erecta* extract can be used to make silver nanoparticles, which can then be used as effective photocatalysts to break down methylene blue. The optimal conditions for methylene blue degradation were achieved at pH 4 with 15 mL of AgNP and 30 minutes of irradiation. The photodegradation process under these conditions reduced the methylene blue concentration by 72.46% from its initial concentration of 100 ppm.

Conflict of Interest

The authors declare that there is no conflict of interest.

Acknowledgements

The authors would like to thank Mrs. Wiji Rahayu of PT. DKSH Jakarta for her kind assisstance in analyzing our samples using PSA.

References

Aksono, E.B., Latifah, A.C., Suwanti, L.T., Haq, K.U., and Pertiwi, H. (2022). Clove Flower Extract (*Syzygium aromaticum*) Has Anticancer Potential Effect Analyzed by Molecular Docking and *Brine Shrimp Lethality Test* (BSLT). *Vet. Med. Int*., 1-7.

Alkadasi, A., Idris, A., Saed, K. and Guan, C.T. (2004). Treatment of Textile Wastewater by Advanced Oxidation Processes. *Global Nest the Int. J. 6*, 222-230

Bere, M.L., Sibarani, J., Manurung, M. (2019). Sintesis Nanopartikel Perak (NPAg) Menggunakan Ekstrak Air Daun Kemangi (*Ocimum Sanctum Linn*.) dan Aplikasinya Dalam Fotodegradasi Zat Warna Metilen Biru. *Cakra Kimia (Indonesian E-Journal of Applied Chemistry)*. *7*(2), 155-164

Choi, H. J., and Yu, S. W. (2019). Biosorption of Methylene Blue from Aqueous Solution by Agricultural Bioadsorbent Corncob. *Environmental Engineering Research*. *24*(1), 99–106.

Dae-Hee A., Won-Seok C., and Tai-Il Y. (1999). Dyestuff Wastewater Treatment Using Chemical Oxidation, Physical Adsorption and Fixed Bed Biofilm Process. *Process Biochemistry*. *34*, 429-439

Gong, Y., Liu, X., He, W.-H., Xu, H.-G., Yuan, F., dan Gao, Y.-X. 2012. Investigation into the Antioxidant Activity and Chemical Composition of Alcoholic Extracts from Defatted Marigold (*Tagetes Erecta L*.) Residue. *Fitoterapia. 83*, 481–489

Harbone. (1987). *Metode Fitokimia Penuntun Cara Modern Menganalisi Tumbuhan. Kosasih Padmawinata*. a.b. Iwang Soediro. ITB. Bandung

Haryani, Y., Kartika, F.G., Yuharmen, Putri, M.E., Alchalish, T.D., Melanie, Y. (2016). Pemanfaatan Ekstrak Air Rimpang Jahe Merah (*Zingiber Officinale Linn Varrubrum*) pada Biosintesis Sederhana Nanopartikel Perak. *Chemica et Natura Acta. 4*(3), 151-155.

Huang, X., Gao, W., Yun, X., Qing, Z., Zeng, J. (2022*). Molecules*, *27*(9), 2865;

Kumar, A. dan Pandey, G. (2017). A Review on the Factors Affecting the Photocatalytic Degradation of Hazardous Materials. *Material Science & Engineering International Journal, 1*(3), 1-10.

Lestari, G.A.D., Suprihatin, I. E., dan Sibarani, J. (2019). Sintesis Nanopartikel Perak (NPAg) Menggunakan Ekstrak Air Buah Andaliman (*Zanthoxylum acanthopodium* DC.) dan Aplikasinya pada Fotodegradasi Indigosol Blue. *Jurnal Kimia Sains dan Aplikasi*. *22*(5), 200-205

Nurhasni, Hendrawati, dan Saniyyah N. (2014). Sekam Padi untuk Menyerap Ion Logam Tembaga dan Timbal dalam Air Limbah. *Jurnal Kimia Valensi*. *4*(1), 36-44.

Salazar-Rabago, J. J., Leyva-Ramos, R., Rivera-Utrilla, J., Ocampo-Perez, R., & Cerino-Cordova, F. J. (2017). Biosorption mechanism of Methylene Blue from aqueous solution onto White Pine (Pinus durangensis) sawdust: Effect of operating conditions. *Sustainable Environment Research*. Vol. *27*(1), 32–40.

Suprihatin, I. E., Lestari, G. A. D., Mardhani, R., and Edoway, V. 2020. Silver Nanoparticles (AgNPs) as Photocatalyst in the Photodegradation of Rhemazol Brilliant Blue. *IOP Conference Series: Materials Science and Engineering, 959*, 1-7.

Suprihatin, I. E., Suat, R.M., dan Negara, I.M.S. (2022). Fotodegradasi Zat Warna Methylene Blue dengan Sinar UV dan Fotokatalis Nanopartikel Perak. *Jurnal Kimia*. *16*(2), 168-173.

Susmanto, P., Gusman, Y., Ridwan, M. F., and Tanara, E. H. (2020). Charactrization of $Cr/SiO_2/Al_2O_3$ Catalyst from Rice Husk Using Impregnation Method. *IJCA (International Journal of Chemical Analysis). 3*(1), 33-39.

Zare-Bidaki, M., Aramjoo, H., Mizwari, Z. M., Mohammadparast-Tabas, P., Javanshir, R., and Mortazavi-Derazkola, S. (2022). Cytotoxicity, antifungal, antioxidant, antibacterial and photodegradation potential of silver nanoparticles mediated via *Medicago sativa* extract. *Arabian Journal of Chemistry*, *15*(6), 1-14.

Zielinska, A., Skwarek, E., Zaleska, A., Gazda, M., and Hupka, J. (2009). Preparation of Silver Nanoparticles with Controlled Particle Size. *Procedia chemistry*, *1*, 1560-1566.