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# Electrosynthesis of Silver Nanoparticle Using Green Tea Leaf Extract and Photocatalytic Methylene Blue Dye Degradation

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**ABSTRACT**

The high toxicity of synthetic dyes poses environmental and health risks, prompting the development of catalysts that improve degradation efficiency, particularly those that support sustainable wastewater treatment. AgNPs have extraordinary catalytic capabilities, making them effective at converting methylene blue (MB) dyes into less hazardous compounds. In this study, AgNPs were synthesised utilising tea leaf extract via electrolysis, providing a sustainable green chemistry strategy with excellent AgNP properties for degrading MB for a brief time. Using two pure silver electrodes and a green tea extract solution as an electrolyte, spherical AgNPs with a surface charge of -20 mV were produced. Tea extract biomolecules serve as bioreductors and capping agents, resulting in the formation of tiny, homogenous, and stable particles maintained until 15 weeks. The small size increases the surface-to-volume ratio along with electrical conductivity, which improves catalytic activity. HPLC analysis revealed that MB degradation reached 96.99% under sunlight for 72 min. Hence, this synthesis technique offers great opportunities for utilising AgNP-based nanocatalysis in wastewater treatment and environmental protection.

## 1. Introduction

Water pollution caused by dyes is a major global issue, consistent with the fast rise of industries that use colours containing specific components. Commonly, the industrial dyes used are azo, anthraquinone, chromophore, formazan, and others [1]. Pollution with azo dyes, particularly methylene blue (MB), has recently gained attention due to the severity of pollution caused by MB in the environment. MB can have various negative consequences. In humans, acute MB exposure can cause an increase in heart rate, vomiting, shock, the formation of Heinz bodies, cyanosis, jaundice, quadriplegia, and necrotic tissue [2]. Some of these consequences highlight the importance of removing MB from water to develop a sustainable society.

Waste can be processed in several ways, including adsorption, flocculation, biodegradation, and decolorisation [3-5]. Adsorption is the most prevalent and widely utilised waste treatment approach due to its low cost, simplicity, ease of use, and suitability for harmful compounds [6]. However, the

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adsorption process has recycling limitations, and adsorbed chemicals can be desorbed if the adsorbent is not handled soon. The adsorption process is greatly influenced by pH, temperature, and contact time, particularly the adsorbent dose, which ignores the low cost. Photodegradation converts dye chemicals into harmless substances such as $H_2O$ and $CO_2$ [7]. The photodegradation approach requires a catalyst in the form of metal nanoparticles, such as AgNP [8]. Surface plasmon resonance (SPR) in AgNPs lets them adsorb more light, creating many positive holes and electrons, and superoxide and hydroxyl radicals. This makes it easier for organic pollutants to break down into less harmful substances [9-11].

Several previous investigations explored the AgNP utilisation for photocatalytic destruction of environmental pollutants. Eco-friendly AgNPs synthesised with *Coleus Vettiveroids* leaf extract demonstrated exceptional photocatalytic degradation characteristics in the reduction of MB dye; within 3 hours of exposure to sunshine, MB dye was 70% degraded [12]. Furthermore, green production of AgNP utilising pomegranate (*Punica granatum*) peel extract and its application in photocatalytic degradation of methylene blue (MB) dye could break down almost 89% of MB dye in 48-72 hours under sunlight irradiation [13]. Furthermore, the photocatalytic activity of green synthesis of AgNP utilising *Morinda tinctoria* leaf extract decreased gradually with increasing exposure time to MB, indicating photocatalytic degradation of MB dye with a degradation efficiency of 95.3% at 72 h [14]. Photodegradation of dye waste is a well-established, simple, and cost-effective technique that yields no harmful byproducts. Photocatalytic dye degradation with AgNPs and sunlight is one of the most environmentally benign methods [15].

Using green tea extract, AgNPs were synthesised for this purpose. Green tea leaves, which have been identified for their high content of various phytochemical elements, are regarded as a promising method for the production of nanoparticles due to their outstanding properties and high reduction potential [16]. Plant metabolite biomolecules such as flavonoids, terpenoids, polyphenols, and proteins have an important role in the reduction of metal ions into nanoparticles [17]. These biomolecules are also responsible for the stability of the produced nanoparticles [18]. Unfortunately, the conventional approach of employing green tea extract has limits due to the lengthy procedure and difficulty in scaling up production. Meanwhile, electrolysis approaches are currently considered a promising approach to directly producing high-quality pure AgNPs [19,20]. The Ag rod electrode serves as an essential precursor for producing AgNPs in this approach [21,22]. Ag rod electrodes are anodically arranged to produce $Ag^+$, which is then reduced to $Ag^0$ in a metal salt electrolyte [23]. Based on the advantages and disadvantages of both biosynthetic and electrochemical procedures, the method described in this work is to synthesise AgNP utilising a simple green electrochemical process with Ag rod electrodes and green tea extract as reducing agents. Using green tea extract solution in electrolysis reduces metal salts, improving time efficiency and product safety. Furthermore, biomolecules in green tea extract prevent Ag aggregation on the cathode surface, increasing its stability. The surface charge generated by these biomolecules plays an important role in determining the efficacy of AgNP application. Considering these issues, this study aims to prepare AgNPs utilising the green electrolysis method and green tea extract as a sustainable approach to AgNP synthesis and their application for photocatalytic degradation of MB dye, which has never been examined before. The characteristics of the resulting AgNPs were determined using UV-Vis spectrophotometry, SEM, PSA, and zeta potential. The redox properties and electrical conductivity of AgNPs were studied. HPLC also observed the effectiveness of MB degradation with increasing incubation time.

## 2. Methodology

### *2.1 Chemicals*

Fresh green tea leaves were purchased from local farms in the Kemuning tea plantation (Karanganyar, Indonesia), while the rest of the chemicals were purchased from Sigma, USA; all the chemicals were extra pure and of an analytical grade. Two Ag rods as electrodes (Ø 1.8 mm with purity 99.9%) were purchased from Antam, Indonesia. Double distilled water was used for all the experiments.

### *2.2 Electrosynthesis of AgNP and its Characterisation*

The green electrolysis method with green tea extract solution as an electrolyte was described by Hermanto, *et al.,* [24,25] as the recommended method for producing AgNPs. The optimum conditions for AgNP synthesis by electrolysis follow the previous procedure [25], namely a distance between the two electrodes of 0.5 cm, a reaction time of 2 min, and a concentration of green tea extract of 1% (w/v). Two electrodes (Ø 1.8 mm and l 100 mm) made of high-purity Ag metal and a precursor for producing silver nanoparticles were employed as the cathode and anode. Previously, the Ag metal rods were cleaned and washed before being positioned vertically on top of the electrolytic reactor cover at a distance of 0.5 cm. A solution of green tea extract, which had been made by soaking it in 100 milliliters of hot water for ten minutes and then diluting it to 500 milliliters, was used to dip the Ag metal rod. Green tea extract served as an electrolyte solution, lowering and stabilising the produced AgNP. In a 500 mL beaker, electrolysis was carried out under ambient circumstances using a continuous DC source voltage of 10 V. To prevent precipitate formation during the electrolysis process, intense stirring at 2000 rpm for two minutes and switching the DC polarity between the electrodes every minute are additional essential innovations for the electrolytic production of AgNPs [25]. Once the solution turns brownish yellow, which indicates the formation of AgNP, the electrolysis is stopped, and the solution is stored in dark bottles at 5 °C.

Several instrumentations were employed to characterise the AgNPs that were synthesised utilising a green tea extract solution and electrochemical procedures. A UV-visible spectrophotometer (Spectrophotometer 7809, Labo-Hub, China) was used for measuring the LSPR absorbance of the produced colloidal AgNPs. Microscopic images and particle morphology were analysed using scanning electron microscopy (SEM-EDX) (JEOL-JEM, Japan). AgNP size and zeta potential were determined using a particle size analyser (PSA) and a zeta sizer (Malvern Instruments, UK). AgNP concentrations were measured using atomic absorption spectroscopy (AAS) (Perkin Elmer AAnalyst 400, USA), and their conductivity values were determined using an Amtast EC900 conductometer (China). Before measurement, colloidal AgNPs were purified by centrifugation at 12,000 rpm (Tomy Centrifuge MDX-310, Japan) and freeze-drying (freeze drier Alpha 1-2LDplus with vacuum pump RZ 2.5, Germany).

### *2.3 Photocatalytic MB Dye Degradation Studies*

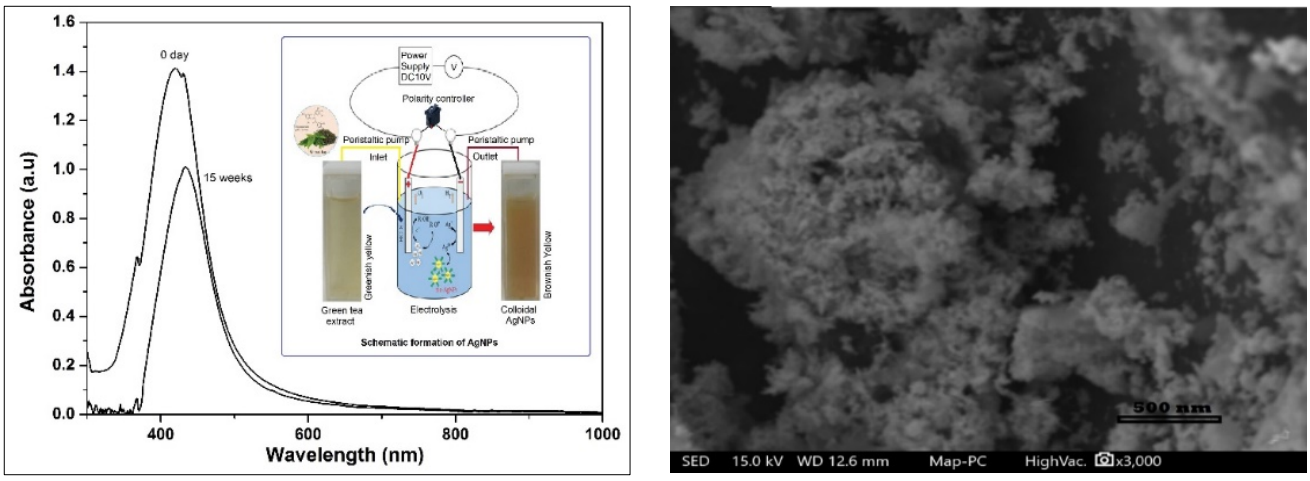
The investigation of dye degradation in aqueous solution allowed the researchers to assess the photocatalytic activity of AgNPs. The light sources used were UV lamps and sunlight. The AgNP colloidal dispersion of 0.5 mL produced from electrosynthesis using green tea extract was combined with 50 mL of MB dye (5 mg/L). Without AgNPs, the control setting was also continuously investigated. To ensure the balance of the working solution, the colloidal aliquot was magnetically stirred at 200 rpm for 10 min in the dark before being irradiated. After the dispersion was exposed

to sunlight, a 3 mL colloidal aliquot was centrifuged at 5000 rpm for 10 min to monitor the photocatalytic activity of the dye degradation. Using high-performance liquid chromatography (Waters Breeze HPLC, USA), equipped with various devices, namely the Waters Delta-60 pump, Waters 600 controller, Waters 2487 Dual Absorbance Detector, and SGE brand column type 250CL4-ODS2-8/5 µm (with length 250 mm, diameter 4 mm, and frit 4/5 µm), the degradation efficiency of AgNPs on MB dye was examined by tracking the decrease in the area of the MB chromatogram [10,26].

## 3. Results and Discussions

The electrolysis method used green tea extract to achieve a sustainable approach to AgNP production. Furthermore, as the process is carried out under ambient conditions, this technique eliminates the need for hazardous precursors and solvents while increasing energy efficiency. The bio-reductant and electrolysis approach for AgNP development involves three steps. During the activation phase (phase 1), electron transfer in the electrochemical system results in the synthesis of RO• radicals from biomolecules (R-OH) of plant extracts, and the release of $Ag^+$ from the electrode to the extract solution as electrolyte. At the growth phase (phase 2), the preparation procedure involves forming a complex between R-O--$Ag^+$ to prevent the formation of Ag oxide due to water electrolysis on the anode surface. The termination phase (phase 3) is the final stage, in which $Ag^+$ is reduced to $Ag^0$, followed by cluster formation and completion for forming AgNPs of a specific diameter and shape; this process occurs quickly. The ability of plant extracts to stabilise formed AgNPs has a significant influence on the termination process [23,25].

The colour of the solution changes rapidly during the electrolysis process, and it turns brownish yellow, indicating that AgNPs were produced, as illustrated in Figure 1a (inset). The LSPR absorption of AgNPs suggests an intense colour. The size and structure of metal nanoparticles influence LSPR, which is defined as the collective excitation of electrons in the conduction band at the surface. The LSPR phenomena can be seen using UV-visible spectroscopy since AgNP's unique optical absorption occurs in the UV-visible spectrum [27]. This LSPR optical phenomenon can be used to determine the formation of AgNPs and their stability during storage, as shown in Figure 1a.

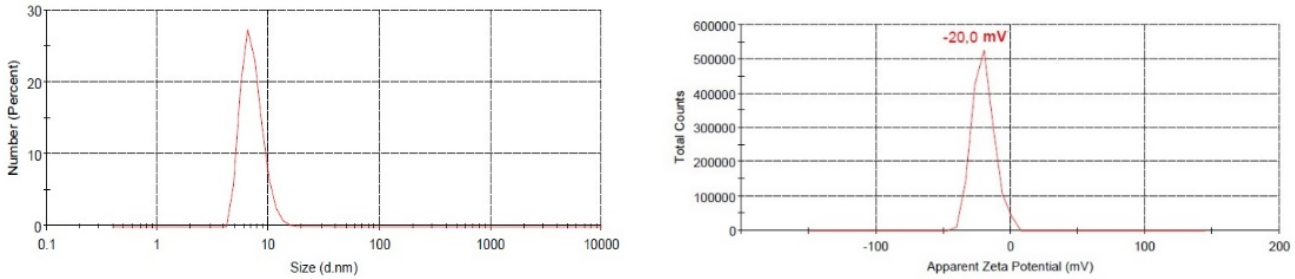



(a) (b)

**Fig. 1**. (a) SPR Spectra of AgNPs at 0 days and 15 weeks of storage (inset) Schematic approach towards the sustainable synthesis of AgNPs via green electrolysis using green tea extract; (b) SEM images of AgNPs

The SEM profile of the synthesised AgNPs at 3000× magnification and an accelerated voltage of 15 kV is depicted in Figure 1(b). The SEM image shows that AgNPs are spherical in clusters, but one particle can be distinguished from another. The role of biomolecules from tea extracts is to cover the particles to prevent aggregation. It suggests that the biomolecules are responsible for maintaining the stability of the formed AgNPs. The stability of the AgNP synthesised in this study was good at the 15th week of storage, as shown in Figure 1a.

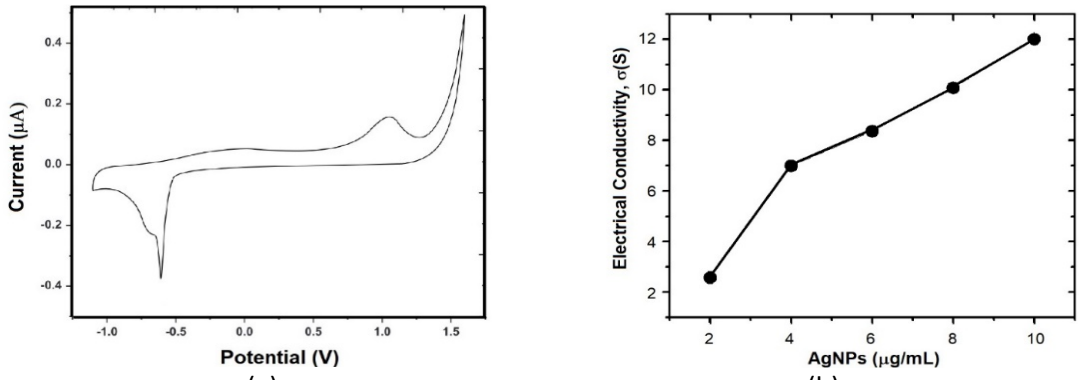
A particle size analyser (PSA) measures particle sizes from 0.1 nm to 10 µm using the dynamic light scattering (DLS) method. It uses infrared scattering to induce Brownian motion, which is the random motion of microscopic particles caused by molecule collisions in AgNP solution [28]. PSA may be used to assess the average size of the distribution of synthesised AgNPs (Figure 2a), which shows the distribution graph and features of AgNP colloid homogeneity. The average size distribution of AgNPs was 7.24 ± 1.71 nm. The size of these nanoparticles is quite small since the natural biomolecules of green tea extract have restrictions in generating a single layer covering particles in solution. This implies that green tea extract is an excellent capping agent.




(a) (b)

**Fig. 2**. (a) Particle size analyzer of AgNPs; (b) Zeta potential of AgNPs

AgNPs are designed to have a narrow distribution range; in other words, the homogeneity is excellent. A high PDI number indicates considerable heterogeneity, whereas a value around zero indicates uniform particle size. The PDI of 0.283 suggested homogeneous nanoparticles were produced. Figure 2b shows the zeta potential for the synthesised of AgNPs. The zeta potential is near zero, and particles tend to aggregate. The synthesised of AgNPs had a moderate negative value of -20 mV, indicating that they are well-dispersed due to particle repulsion. Green tea leaf biomolecules provide AgNPs with a negative surface charge, resulting in interparticle repulsion when two or more particles are close together. This repulsion keeps the AgNP from aggregating, keeps it small, and ensures high stability for up to 15 weeks in storage. A stability test using SPR spectra up to 15 weeks of storage confirmed AgNPs' moderate stability (Figure 1a).




(a) (b)

**Fig. 3**. (a) Cyclic voltammetry of AgNPs; (b) electrical conductivity of AgNPs

The green tea extract mediating AgNP synthesis exhibited redox properties according to the cyclic voltammetry profile of biosynthetic AgNPs, as shown in Figure 3a. Cyclic voltammetry measurements were carried out using a three-electrode system. The working electrode is a glass carbon electrode with an Ag/AgCl electrode as a reference. The stainless wire serves as an additional electrode. The voltammetric scanning speed is 0.5 $mVs^{-1}$ under ambient conditions in the range of -1.5 to 1.5 V. According to previous work, the cyclic voltammetry profile shows an anodic current (oxidation peak) at 1.0 V, indicating the presence of a biomolecule (R-OH). At the same time, a peak potential of -0.6 V confirmed the characteristic peak of AgNPs in the cathodic current (reduction peak). In this cyclic voltammetry profile, a decrease in the peak of the anodic wave or disappearance after the biosynthesis of AgNPs is possible. In this work, the cyclic voltammetry profile indicated that biomolecular components interacted with metal ions ($Ag^+$) through their functional groups to form intermediate complexes (R-O--$Ag^+$) and mediate reduction to nanoparticles ($Ag^0$). This is in line with the formation process of AgNPs using the bio-reductant and electrolysis method [25,29].

The effect of AgNPs on electrical conductivity was also analysed, as shown in Figure 3b. The concentration of AgNPs for this purpose was determined using AAS. There is a linear relationship between the concentration of AgNPs and their electrical conductivity; it can be used quantitatively in determining the formed AgNPs during electrolysis. The conductivity values of the synthesised AgNPs with a concentration range of 2-10 µg/mL were obtained from 2.3 to 11.8 S; similar values were reported by a previous study, indicating the high electrical conductivity of AgNP obtained. Stabilising silver (Ag) particles with a capping agent commonly reduces the electrical conductivity due to the covering layer that isolates and insulates Ag particles in the matrix. In this study, the biomolecular thin layer of green tea extract stabilising AgNPs with electron-rich functional groups [25] allows adjacent Ag particles to create an interconnected conductor of the surrounding dielectric. The excellent electrical conductivity of synthesised AgNPs is attributed to their large and homogeneous specific surface area, as well as the biomolecular thin layer surrounding their surface.

Photocatalysis is a chemical reaction process facilitated by light and a solid catalyst, as illustrated in Figure 4. The light will produce electrons and holes ($e^-$ and $h^+$). Then, electrons react with oxygen in the water to create anion radicals ($\bullet O_2^-$), which significantly oxidise hydroxyl radicals (•OH). While holes oxidise dissolved hydroxyl to produce high-energy radicals. High-energy hydroxyl radicals can degrade organic pollutants (MB dye) in liquids into $CO_2$ and $H_2O$, which then evaporate or transform into harmless molecules [30,31].

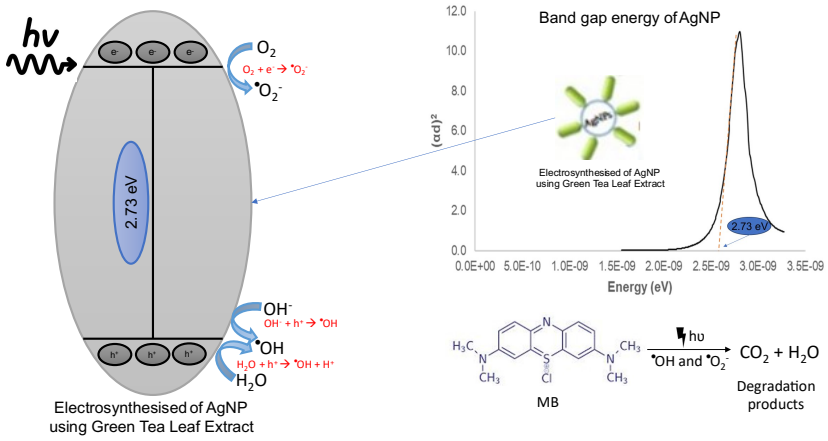



**Fig. 4.** Photocatalytic Methylene Blue Dye Degradation (inset band gap energy of AgNP)

Electrosynthesised AgNPs using green tea leaf extract have hydrophilic ability on the surface of AgNPs as the performance of biomolecules that become stabilising agents of AgNPs formed. AgNPs have a negative surface charge due to green tea leaf biomolecules (in Figure 2a); it is beneficial in the ability to adsorb more •OH. Furthermore, the electrosynthesis of AgNP using green tea leaf extract results in a low energy band gap of 2.73 eV (Figure 4), which is smaller than prior work [11]. A low energy gap facilitates particle transitions from the valence band to the conduction band, but it is also susceptible to recombination. The jump produces an empty state known as a hole. The hole oxidises water adsorbed on the surface of AgNP, producing •OH. The •OH interacts with organic molecules, converting them into $CO_2$ and $H_2O$. The smaller the energy gap, the easier it is to generate •OH and the greater the photocatalytic activity in degrading MB dye.

HPLC studied dye degradation before and after photocatalytic degradation. Figure 5 shows that the peak of MB dye occurs at a retention time (Rt) of 1.6-2.0 min.

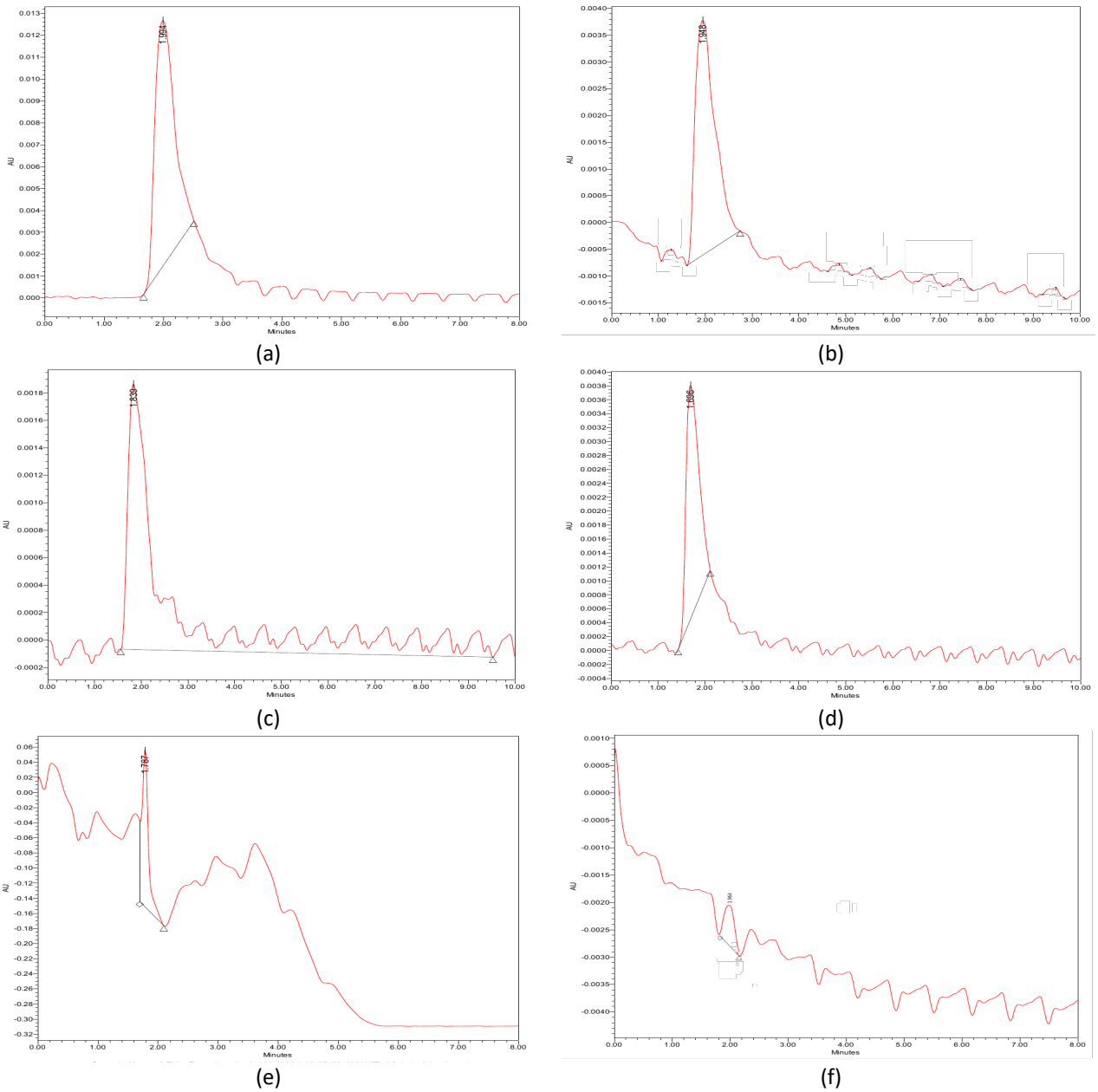



**Fig. 5**. HPLC analysis of methylene blue (a); after dye degradation by electrosynthesised AgNPs (5 mg) using UV-lamp for 1 h (b); using sunlight for 1 min (c); 24 min (d); 48 min (e); and 72 min

HPLC was used to evaluate the photocatalytic degradation of MB dye by electrosynthesised AgNPs containing green tea leaf extracts. The aqueous MB solution was prepared using water eluent. Figure 4a shows the chromatogram for the MB solution before the addition of AgNPs. The chromatogram for the MB solution following the addition of AgNPs is shown in Figure 4b-f. The dye degradation process was performed three times. According to Figure 4 and Figure 6, electrosynthesised AgNPs containing green tea leaf extract may perform photocatalytic degradation activity against MB at various time intervals utilising sunlight, with the highest percentage of dye degradation (96.99%) achieved after 72 min. The oxidation process underlies the occurrence of dye degradation. The absorption peak for MB dye is displayed on the chromatogram with a retention time based on previous data (Figure 4a). Finally, the peak disappears while the reaction time increases, meaning the dye has been degraded. The oxidation process has been completed and is detected by changing the color of the reaction mixture to colorless. In addition to the help of sunlight, the degradation process of MB dyes can also be carried out under set conditions, namely using a UV lamp. However, the results are still better using sunlight.

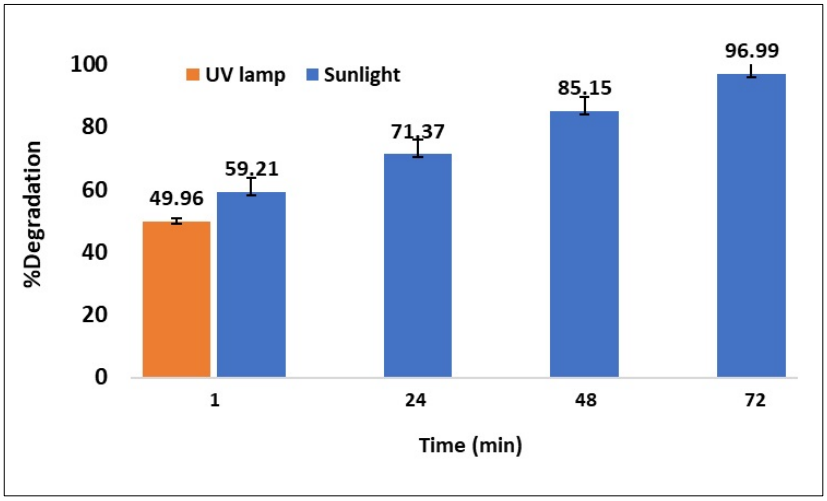



**Fig. 6**. Photocatalytic degradation activity of MB by AgNPs in various time intervals

According to the literature, sunlight (photons) interacts with AgNP and excites electrons from the valence band to the conduction band, resulting in electron-hole pairs. Simultaneously, dye molecules interact with photons and become excited, increasing in the number of electrons in the system [15]. Since green tea leaf extract acts as a stabilising/capping agent on electrosynthesised AgNPs, AgNPs have high conduction properties, allowing electrons produced by this photo process, both from AgNPs and MB dyes, to be easily transferred to the surface of the AgNP capping. An oxidation process occurs, in which photo-induced electrons are captured by atmospheric oxygen (AgNP capping) to form oxygen anion radicals. At the same time, electron-hole recombination prevents photogenerated holes by converting electrons from hydroxyl anions into hydroxyl radicals. These radicals can break down MB into carbon dioxide, water, and smaller organic molecules or ions. AgNPs have a negative surface charge because green tea leaf biomolecules (atmospheric oxygen) act as capping agents with a large specific surface area, which might expedite dye reduction and hence increase degradation efficiency [32,33]. Table 1 compares the efficiency of AgNPs in degrading MB in our investigation with earlier studies. In general, this study's percentage degradation outperformed earlier research with a shorter incubation period. The specific surface area is greater and more effective in promoting electron transfer and oxidative processes due to the smaller and more uniform size. In addition, the low band gap energy value also contributes to this advantage.

**Table 1**
Comparison of Effectiveness of Synthesised AgNPs in Degrading MB

| Synthesis method | Bioreductor & capping agent | Size (nm) | Time | %Degradation | Ref. |
|---|---|---|---|---|---|
| Biosynthesis | *Peltophorum pterocarpum* leaves | 2-50 | 6 min | 82 | [32] |
| Biosynthesis + UV | *Coleus Vettiveroids* leaves | 10-50 | 3 h | 70 | [12] |
| Biosynthesis | Camellia sinensis leaves | 25-40 | 72 h | 95 | [8] |
| Biosynthesis | Natural honey | 5-25 | 72 h | 92 | [10] |
| Biosynthesis | Punica granatum peel | 57.7-142 | 72 h | 89 | [13] |
| Biosynthesis | *Morinda tinctoria* leaves | 79-96 | 72 h | 95 | [14] |
| Electrosynthesis | Green tea leaves | 7.24±1.71 | 72 min | 96.99 | This study |

Despite AgNP showing outstanding performance in dye degradation, its discharge into the environment offers a potential concern to both human health and environmental safety. Whereas AgNPs are less hazardous than silver ions, their potential transformation into other chemical forms, such as $Ag^+$ ions, can be damaging to the aquatic environment. Therefore, establishing strategies to reduce nanoparticle leakage into the environment is crucial. Sulfidation is an additional handling strategy that can be utilised to mitigate this effect by turning AgNP into less dangerous silver sulphide [34].The coagulation-flocculation process can also aggregate AgNP into larger particles that settle and are easily separated by filtering [35,36]. The goal is to prevent AgNP's harmful impacts on the environment and human health while maintaining its outstanding performance in degrading MB.

## 4. Conclusions

The green electrolysis approach has been employed with green tea leaf extract for producing AgNPs with enhanced abilities to break down or degrade MB. Tea leaf extract biomolecules play an important role in the action of bioreductants and capping agents, resulting in spherical nanoparticles with a very small and uniform size of roughly 7.24 nm, a surface charge of -20 mV, and a PDI of 0.283. These properties allow nanoparticles to maintain excellent stability over lengthy periods of storage. The catalytic activity of synthesised AgNPs in degrading MB is enhanced by their narrow energy gap (2.73 eV), high electrical conductivity, and small size that increases the surface-to-volume ratio. HPLC study revealed degradation efficiency up to 96.99% after 72 min of exposure to sunlight. As a result, photocatalytic dye degradation utilising AgNPs synthesised by the green electrolysis approach is a promising solution for environmentally friendly and sustainable waste management.

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