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Fabrication of *Pinus pinaster*'s Tannin-Engineered Silver Nanophotocatalyst for Degradation of Methylene Blue Dye

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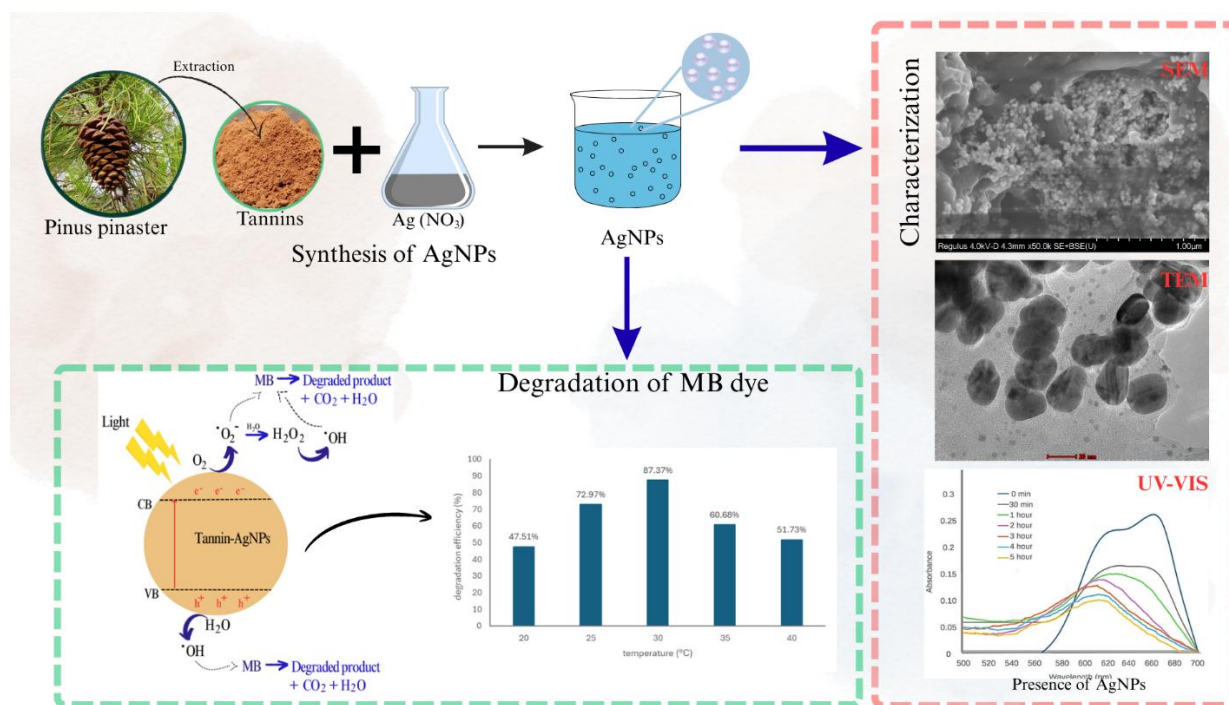
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Abstract

The increasing demand for sustainable nanomaterials has driven the development of green synthesis strategies that replace conventional toxic reagents with renewable bioresources. Plant-derived phytochemicals provide an eco-friendly pathway for fabricating functional nanoparticles for environmental applications. Therefore, in this study, silver nanoparticles (AgNPs) were synthesized via a green approach using tannins extracted from *Pinus pinaster* as natural reducing and stabilizing agents, thereby eliminating the need for hazardous chemicals. The formation of *Pinus pinaster*'s tannin mediated AgNPs (PPT-AgNPs) was confirmed through UV–visible spectroscopy, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDX), and transmission electron microscopy (TEM). The microscopy studies revealed that AgNPs particle sizes ranged from 15.9 to 96.4 nm. The photocatalytic activity of the synthesized AgNPs was evaluated for the degradation of methylene blue dye under UV irradiation. The photocatalytic reaction deviates from classical Arrhenius kinetics but may be governed by a balance between molecular kinetics, adsorption/desorption equilibrium and/or charge carrier recombination rates. Optimum conditions were achieved at pH 5 and 30°C, reaching a degradation efficiency of 87.37% within 5 h. Kinetic analysis showed that the degradation followed pseudo-first-order kinetics with a rate constant of 0.4961 h⁻¹. Overall, the utilization of *Pinus pinaster* tannins as natural reducing and stabilizing agents provides a sustainable route for AgNP fabrication, yielding photocatalysts with promising activity for wastewater treatment applications.

Keywords: *Pinus pinaster* tannins; green synthesis; silver nanoparticles; photocatalyst, degradation of methylene blue

Graphical Abstract



1. Introduction

Nanotechnology has emerged as a rapidly advancing field due to the unique physico-chemical properties of materials at the nanoscale. Nanoparticles are typically materials with dimensions below 100 nm, and their small size provides distinctive characteristics compared with bulk materials. One of the most important features of nanoparticles is their high surface area-to-volume ratio, which significantly influences their chemical reactivity and interactions with surrounding substances[1]. Because of these properties, nanoparticles have found widespread applications in various fields, including catalysis, water purification, healthcare, and agriculture[2]. Nanoparticles can be classified based on their composition, structure, size, and morphology, with common types including carbon-based, metallic, ceramic, semiconductor, polymeric, and lipid-based nanoparticles [1], [3].

Among these, metallic nanoparticles have attracted significant scientific attention due to their remarkable optical, catalytic, and antimicrobial properties[4]. In particular, silver nanoparticles (AgNPs) are widely recognized for their strong antimicrobial activity against a

broad range of microorganisms, including bacteria, viruses, and fungi [5], [6]. These properties have led to their extensive use in antibacterial coatings, textiles, medical devices, and consumer products[7]. In addition to biomedical applications, AgNPs have demonstrated excellent catalytic performance in several chemical reactions, including the reduction of nitroaromatic compounds and various oxidation and hydrogenation reactions [8]. Their small size and high surface reactivity provide abundant active sites that enhance catalytic efficiency.

Recently, AgNPs have also attracted increasing interest for environmental applications, particularly in wastewater treatment. Industrial effluents from textile, pharmaceutical, and dye manufacturing industries often contain large amounts of synthetic dyes that are toxic and resistant to biodegradation [9]. Among these pollutants, methylene blue (MB) is widely used and frequently detected in wastewater streams. Its persistence and toxicity pose serious environmental and health concerns. Photocatalytic degradation has emerged as a promising method for removing such pollutants from contaminated water. AgNPs exhibit photocatalytic activity under light irradiation, generating reactive oxygen species (ROS) such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide anions ($\text{O}_2^{\bullet-}$), which can effectively degrade dye molecules into less harmful products[11],[12]. These properties make AgNPs attractive candidates for environmentally friendly wastewater treatment technologies.

AgNPs can be synthesized through several approaches, generally categorized into top-down and bottom-up methods [12]. Physical methods, such as laser ablation, represent top-down approaches in which bulk materials are broken down into nanoscale particles. Although these techniques produce highly pure nanoparticles, they often require expensive equipment and high energy consumption, limiting their scalability [13]. Chemical synthesis, which follows a bottom-up approach, is more commonly used and involves reducing silver ions (Ag^+) from silver salts such as AgNO_3 using chemical reducing agents like sodium borohydride or ascorbic acid. Stabilizing agents are also required to prevent nanoparticle aggregation and control particle size [14]. However, these chemical methods frequently involve toxic reagents and may generate hazardous byproducts, raising environmental and safety concerns.

To overcome these limitations, green synthesis approaches have gained increasing attention as sustainable alternatives for nanoparticle production. Green synthesis utilizes biological resources such as plant extracts, bacteria, fungi, and algae to reduce metal ions into nanoparticles [15]. Plant extracts are particularly attractive because they contain abundant phytochemicals such as polyphenols, flavonoids, tannins, alkaloids, and terpenoids that can act as both reducing and stabilizing agents [16]. These biomolecules facilitate the conversion of Ag^+

into metallic AgNPs while simultaneously stabilizing the particles, resulting in environmentally friendly, biocompatible, and stable nanomaterials [17], [18]. Furthermore, the size and morphology of the synthesized nanoparticles can be tuned by adjusting synthesis parameters such as pH, temperature, and extract concentration [19].

Among various plant-derived compounds, tannins have shown great potential for green nanoparticle synthesis due to their strong antioxidant and reducing properties. Tannins are naturally occurring polyphenolic compounds widely found in plants and are capable of donating electrons to reduce metal ions into nanoparticles [20]. One promising source of tannins is *Pinus pinaster*, commonly known as maritime pine. This Mediterranean conifer contains a wide variety of bioactive compounds, including flavonoids and phenolic acids such as catechin, quercetin, cinnamic acid, and taxifolin, which exhibit strong antioxidant properties [21], [22]. These compounds make *Pinus pinaster* a potential natural resource for the eco-friendly synthesis of AgNPs. Previous studies on related pine species have demonstrated the feasibility of using pine bark extracts for nanoparticle production. For instance, Iravani and Zolfaghari[23] successfully synthesized spherical AgNPs ranging from 10 to 40 nm using *Pinus eldarica* bark extract, while Velmurugan et al. [24] reported the synthesis of antibacterial AgNPs using extracts from *Pinus densiflora* cones.

In addition to their antimicrobial properties, green-synthesized AgNPs exhibit promising photocatalytic activity for the degradation of organic dyes. Several studies have reported the effective removal of MB using AgNPs synthesized from plant extracts such as *Magnolia kobus*, *Azadirachta indica*, *Moringa oleifera*, and *Aloe vera* [23], [25], [26], [27]. These nanoparticles exhibit enhanced photocatalytic performance due to their nanoscale size, high surface reactivity, and strong surface plasmon resonance, which improves light absorption and electron transfer processes [28]. Despite these advances, studies on the green synthesis of AgNPs using *Pinus pinaster*'s tannins and their application in photocatalytic dye degradation remain limited. Therefore, this study aims to synthesize AgNPs using *Pinus pinaster* tannins as natural reducing agents and to evaluate their photocatalytic performance in the degradation of MB under UV irradiation. The findings are expected to contribute to the development of sustainable nanomaterials for environmental remediation, particularly in wastewater treatment applications.

2. Experimental

2.1. Materials and chemicals

Tannin was extracted from the bark of *Pinus pinaster* (Maritime Pine) with slight modification as reported elsewhere [29]. In short, the ground *Pinus pinaster* bark powder was immersed in 80°C water containing 2.5% of Na₂CO₃ and 2.5% of Na₂SO₃ (m/m based on the weight of dried bark powder) for 4 h. After filtration, the resulting aqueous fraction was spray-dried, and the extract obtained was used for analysis. Silver nitrate (AgNO₃) was purchased from R&M Chemicals SDN BHD, Malaysia. In order to study photocatalytic degradation, MB dye was employed. For the qualitative analysis, isopropanol, ascorbic acid, and EDTA were used as received, without any further purification.

2.2. Green synthesis of PPT-AgNPs

A 100 mL solution of 1000 ppm *Pinus Pinaster*'s tannin and a 100 mL solution of 1000 ppm AgNO₃ were prepared in two different volumetric flasks. After mixing 50 mL of each solution in a 100 mL volumetric flask, the mixture was thoroughly stirred with a magnetic stirrer at room temperature (30 ± 2 °C). The transformation of Ag⁺ into AgNPs was demonstrated by a change in the reaction mixture's colour intensity, which indicated the presence of AgNPs [30]. To ensure complete reactivity and stabilisation of the nanoparticles, the solution was shaken for 48 hours. To separate the nanoparticles, the mixture was centrifuged for 20 minutes at 6000 rpm after being shaken. The upper solution, referred to as the supernatant, was carefully decanted, while the colloidal PPT-AgNPs in the lower layer were collected and used in subsequent studies. A schematic of the overall synthesis process is shown in **Figure 1**.



Figure 1: Overall methodology of preparation of PPT-AgNPs

2.3. Spectroscopy and Microscopy Characterization

The physicochemical and morphological properties of the green PPT-AgNPs catalyst were comprehensively investigated using a series of advanced characterization techniques. The Shimadzu UV-2600 ultraviolet-visible (UV-Vis) spectrophotometer was used to confirm the presence of AgNPs initially. The UV-Vis sensitivity of the PPT-AgNPs samples was evaluated between 300 and 700 nanometres (nm). To track the formation and evolution of PPT-AgNPs, measurements were made at various time intervals. This enabled consistent observation of the distinctive surface plasmon resonance (SPR) peak associated with PPT-AgNPs, demonstrating that the nanoparticles remained stabilized over the long term and that Ag^+ were reduced.

The process of creating PPT-AgNPs was analyzed and described using the Shimadzu IR Spirit FT-ATR spectrometer. To get rid of any contaminants, the ATR crystal surface was cleaned with ethanol. A small amount of the material was deposited onto the ATR crystal's surface and the samples' spectra were obtained in the range of $4000 - 400 \text{ cm}^{-1}$.

Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX), was utilized to determine the morphology and elemental composition of the sample. The PPT-AgNPs were placed on an aluminium planchette. Then, it was dried overnight at $50 - 60^\circ\text{C}$ in an oven before analysis.

The size, shape, and distribution of the samples were measured using the Technai G2 20 S-Twin transmission electron microscopy (TEM). A single drop of PPT-AgNPs was placed on a carbon-coated copper grid, followed by drying at room temperature. AgNPs sizes were quantified, and their images were visualised.

To determine the point of zero charge (pH PZC), 30 ml of ultrapure water was placed in beakers, and the initial pH was adjusted from 2 to 10 using 0.1 M NaOH and 0.1 M HCl solutions. Subsequently, the solutions were combined with the 50 μ L of PPT-AgNPs, and the resulting mixture was agitated at the minimum speed to serve as a shaker. The pH of the solutions was measured 24 hours later, and the overall pH was determined by subtracting the initial pH from the final pH. The data on the initial pH were plotted, and the pH at the PZC of the sample was determined as the intersection of the curve with the x-axis.

2.4. Photocatalytic Degradation of MB by PPT-AgNPs Mixture

The photocatalytic degradation experiments were conducted by mixing 50 mL of 2×10^{-5} M MB solution with different volumes of PPT-AgNPs (6, 8, and 10 mL). Distilled water was added to maintain a constant total volume, as summarized in Table 1. The mixture was stirred to ensure uniform dispersion of the nanoparticles. Before UV irradiation, the solution's initial absorbance was measured by UV–Vis spectrophotometry over 500–700 nm. The solution was then exposed to UV light for 5 h under continuous stirring. Absorbance measurements were taken at 30 min intervals to monitor the MB degradation. The degradation efficiency was calculated using:

$$\text{Degradation (\%)} = \frac{A_i - A_f}{A_i} \times 100\% \quad [1]$$

where, A_i represents the initial absorbance and A_f represents the final absorbance. A similar procedure was repeated as above for different sets of experiments in which the volume of PPT-AgNPs was varied as tabulated in Table 1.

Table 1: Different sets of volumes of PPT-AgNPs

Sample Denotation	Methylene Blue Solution (mL)	PPT-AgNPs (mL)	Distilled Water (mL)
6* AgNPs	50	6	4
8* AgNPs	50	8	2
10* AgNPs	50	10	0

2.5. Effect of pH on Photocatalytic Degradation of MB.

To examine the effect of pH, 50 mL of MB solution was mixed with 10 mL of PPT-AgNPs, which was first evaluated at pH 5. Additional sets were made by using suitable acidic (HCl) or basic (NaOH) solutions to change the pH to 3, 8, and 9. The baseline absorbance was recorded across 500 – 700 nm before UV light exposure. Each pH-adjusted solution was placed in a separate beaker and exposed to UV light while being continuously stirred to ensure even exposure. To track MB degradation, samples were collected every hour for a total of 5 hours. To determine the optimal pH for maximum photocatalytic activity, the degradation efficiency was calculated for each pH-adjusted solution using equation [1], and the results were compared.

2.6. Effect of Scavenger on Photocatalytic Degradation of MB.

To examine the effect of scavengers, 50 mL of MB solution was mixed with 10 mL of PPT-AgNPs. Next, three different solution mixtures were prepared by adding 1.0 mL of 0.1 M ascorbic acid, 0.1 M isopropanol, and 0.1 M EDTA, each serving as a scavenger. The baseline absorbance was recorded across 500 – 700 nm before UV light exposure. The solution mixture was exposed to UV light while being constantly stirred to guarantee even exposure. To monitor the degradation of MB, samples were collected every hour for a total of five hours. The absorbance of MB was measured at 661 nm using UV-Vis spectroscopy. The percentage of degradation efficiency was computed for each scavenger solution using the formula [1], and the results were compared.

2.7. Effect of Temperature on Photocatalytic Degradation of MB.

To study the effect of temperature, 50 mL of MB solution was mixed with 10 mL of PPT-AgNPs at a temperature of 30°C. Subsequently, the experiment was then carried out at various temperatures: 20°C, 25°C, 35°C, and 40°C. Photocatalytic degradation was monitored similarly as described above. The values of the rate constant were computed for each temperature using the formula [2],

$$\ln \left(\frac{C_0}{C} \right) = kt \quad [2]$$

where, C_0 represents the initial concentration, C represents the final concentration, t represents time in hours, and k represents the rate constant in hours^{-1} .

3. Results and discussion

3.1. Visual Observation

A key visual sign of the formation of PPT-AgNPs is a shift in the color of the reaction mixture, changing from a pale brown (**Figure 2a**) to a dark brown (**Figure 2b**). This color change is due to the surface plasmon resonance (SPR) phenomenon, in which conduction electrons on the nanoparticle surface oscillate in resonance with incident light [31]. In this study, the concentrations of the tannin extract and AgNO_3 solution were adjusted to their optimum values of 1000 ppm to achieve the best results for the characterization and application of the PPT-AgNPs. The resultant PPT-AgNPs were analysed through UV-Vis, FTIR, SEM-EDX, and TEM.

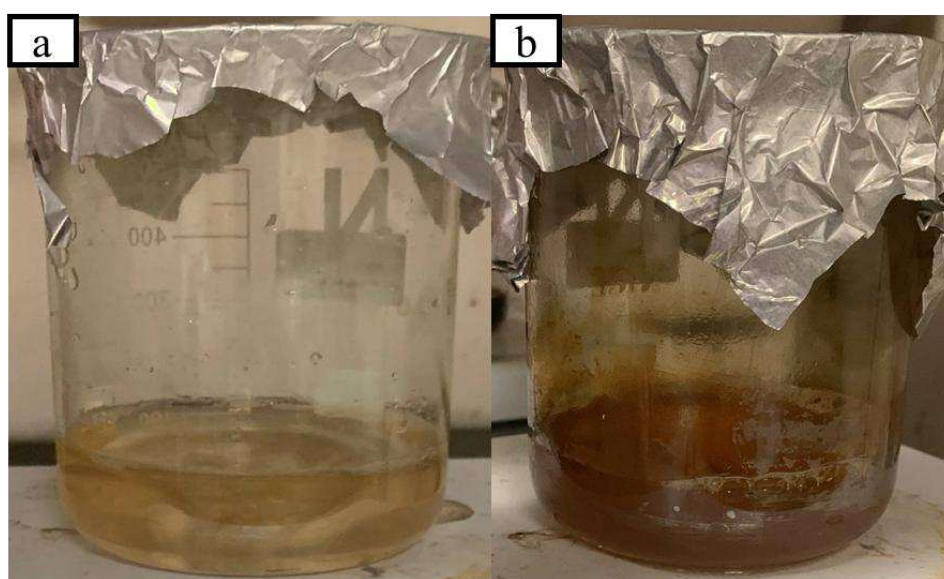


Figure 2: Visual image of AgNO_3 from (a) pale brown to (b) dark brown

3.2. UV-Visible Spectroscopy

The UV-Vis spectra shown in **Figure 3a** provide some captivating insights into the formation and growth of the PPT-AgNPs for over 0 to 48 hours. By measuring the absorbance across a wavelength range of 300 to 700 nm, the evolution of the absorbance profile over time can be clearly observed. At the very beginning (0 minutes), the spectrum displays a broad absorbance without any clear peaks in the visible region, suggesting that well-formed nanoparticles are still absent. However, as the reaction continues, a significant change in the absorbance profile is noticed, especially after just 1 hour, when a new peak begins to appear. This peak becomes increasingly defined, narrow, and intense, ultimately reaching a maximum at 48 hours with a strong, distinct absorbance peak centred at 445 nm.

This peak at 445 nm is characteristic of the surface plasmon resonance (SPR) phenomenon linked to AgNPs [16]. For PPT-AgNPs, this resonance usually falls between 400 and 450 nm, influenced by various factors like particle size, shape, the surrounding dielectric environment, and the extent to which the particles are aggregated [32]. The presence of a sharp SPR peak at 445 nm indicates the successful formation of relatively uniform and well-dispersed spherical AgNPs. Additionally, the peak shifting and sharpening over time indicate that the nanoparticle nucleation and growth are being controlled, resulting in a stable colloidal solution with minimal aggregation [33].

Literature reports are in agreement with these findings. For instance, Verbruggen et al. [34] found that chemically synthesised spherical AgNPs exhibit SPR peaks ranging from 410 to 430 nm, which vary with particle size and the surrounding medium. Similarly, El-Kemary et al. [35] observed SPR peaks at 420-440 nm for AgNPs synthesised using plant extracts, further emphasising that synthesis conditions can affect SPR behaviour. Furthermore, Dogiparthi et al. [16] noted that biologically synthesised AgNPs typically exhibit SPR peaks between 420 and 450 nm. This highlights that while different synthesis methods, whether chemical, biological, or green synthesis, might slightly alter the SPR peak, they generally stay within this typical range. The observed peak at 445 nm in this study falls within the established range, confirming the formation of PPT-AgNPs with the expected optical and structural properties. Moreover, the increasing absorbance intensity over time indicates a higher concentration of nanoparticles as the reaction proceeds, suggesting a successful and gradual synthesis process.

3.3. FTIR spectroscopy

The FT-IR spectra for *Pinus pinaster*'s tannin and PPT-AgNPs highlight the important functional groups that play a role in the formation and stabilization of nanoparticles. As illustrated in **Figure 3b**, the spectra display absorption peaks in the range of 500 to 4000 cm^{-1} , which correspond to the distinct vibrational modes of polyphenolic compounds. A comprehensive summary of the assignments for each wavenumber, along with their corresponding functional group interpretations, can be found in **Table 2**.

Table 2: Wavenumbers present in FT-IR and their functional group for both compounds, *Pinus pinaster*'s Tannin and PPT-AgNPs.

Compound	Wavenumber cm^{-1}	Functional group
<i>Pinus pinaster</i> 's Tannin	3292	O–H stretching
	1610	C=O stretching
	1516	Aromatic C=C stretching
	1438	C–H bending
	1271	C–O stretching
	1092	C–O–C stretching
PPT-AgNPs	3292	O–H stretching
	1610	C=O stretching
	1563	Aromatic C=C stretching
	1462	C–H bending

In both samples, the broad peak at 3292 cm^{-1} is attributed to the O–H stretching from phenolic hydroxyl groups, which are common in tannins. This band is typically broad because of strong hydrogen bonding. Its presence in both spectra indicates that hydroxyl groups remain largely intact, although slight intensity changes may suggest partial involvement in Ag^+ coordination [36]. The notable peak at 1610 cm^{-1} is attributed to C=O stretching of conjugated or Ag^+ -chelated carbonyl groups, as its lower frequency compared to the typical C=O (around 1700 cm^{-1}) suggests some electron delocalization or metal coordination [36]. In the PPT-AgNPs, this indicates a chemical interaction during the formation of AgNPs. In addition, the distinct peak at 1516 cm^{-1} corresponds to aromatic C=C stretching of the polyphenolic aromatic ring. Meanwhile, the peak at 1438 cm^{-1} corresponds to C–H bending vibrations, which are typically observed in aromatic and aliphatic regions. These peaks shifted to 1563 cm^{-1} and 1438 cm^{-1} , and suggest that the changes in intensity and position of these two peaks indicate interaction between the carbonyl groups, aromatic rings, and AgNPs [37].

Notably, only the *Pinus pinaster* tannin spectra show peaks at 1271 cm^{-1} and 1092 cm^{-1} . These peaks are assigned to C–O–C vibrations and C–O stretching, respectively, typical of ethers and alcohols, respectively [21]. From the spectra in **Figure 3b**, it is evident that tannins

not only reduce Ag^+ ions but also stabilise AgNPs formed in this process through coordination with functional groups [20]. The appearance of new bands and subtle shifts in existing peaks, as outlined in **Table 2**, clearly indicate that the formation of nanoparticles brings about specific chemical changes in the tannin structure. These findings confirm that the polyphenolic components of tannin are directly responsible for both the reduction and capping of AgNPs[20]. The result of FTIR analysis confirmed the presence of $-\text{OH}$, $\text{C}=\text{C}$, and CH , indicating the plant extract possesses flavonoids which consist of hydroxyl and carboxyl. These observations highlight the significant role of tannin's functional groups in the chelation and stabilization processes during the formation of AgNPs, with the altered peaks serving as key indicators of successful nanoparticle synthesis.

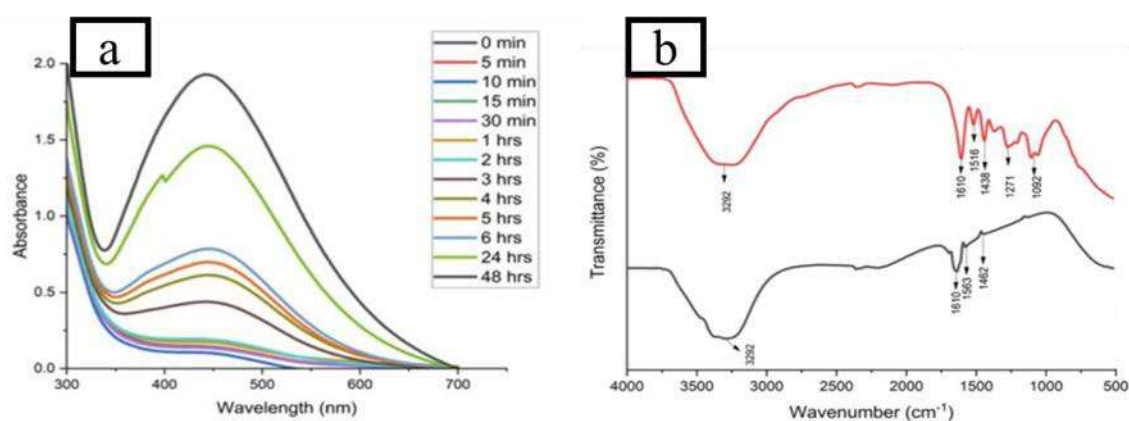


Figure 3: (a) UV-Vis absorbance spectra of AgNPs at different time intervals and (b) FT-IR spectra of *Pinus pinaster*'s Tannins and PPT-Ag-NPs.

3.4. SEM-EDX and TEM analysis

SEM-EDX provides detailed information on both the morphology and elemental composition of the samples [31], [38]. The SEM images shown in **Figure 4a and b** below display PPT-AgNPs magnified at 100k. These particles are mostly spherical or nearly spherical and vary in size from 15.9 nm to 35.4 nm. This size range aligns well with what is typically observed in AgNPs produced by either chemical or green synthesis methods. The particles are well dispersed, with no noticeable aggregation, which supports the formation of stable, distinct nanoparticles. Additionally, the presence of a relatively uniform size distribution confirms the successful synthesis process indicated by UV-Vis analysis.

The EDX spectrum complements the morphological analysis by confirming the elemental composition of the sample (**Figure 4c**). The spectrum clearly shows a dominant peak for Ag, along with smaller peaks for carbon (C), oxygen (O), aluminum (Al), and chlorine (Cl). The atomic percentages are inserted in **Figure 4c**. The high percentage of Ag strongly confirms that Ag is the major component. The presence of carbon and oxygen likely comes from organic molecules, probably from the capping or stabilizing agents used during the synthesis process. As for chlorine, it might be from the Ag precursor salt, while aluminum could be from the sample holder or substrate. The nanoscale size, spherical morphology, and dominant Ag content (over 74%) confirm that the synthesis and stabilization of AgNPs have been achieved.

TEM was used to further characterize the synthesised PPT-AgNPs, specifically focusing on their morphology, size distribution, and structural features. The high-resolution images obtained at a magnification of 195k allow for close examination of the nanoparticles, giving a clear view of their shape and size at the nanometer scale (**Figure 4d and e**).

The TEM analysis showed that the PPT-AgNPs produced with plant extract as a reducing and stabilizing agent were primarily spherical, although some variations in shape were observed, including a few irregular and slightly oval particles. This variety in shape is often linked to biological synthesis methods, in which the phytochemicals from plants play a role in how nanoparticles nucleate and grow [39]. Based on TEM measurements, the diameters of the PPT-AgNPs ranged from 15.0 to 96.4 nm, which aligns more or less with the findings from SEM. This consistency across different characterization methods reinforces the reliability of the synthesis approach and confirms the successful production of nanoparticles with the expected size and shape.

According to Ijaz and Gilani, et al. [3], nanoparticles are materials that have at least one dimension measuring between 1 and 100 nm. The size range noted in this study shows that the synthesised PPT-AgNPs fits this definition. Moreover, research by Dogiparthi et al. [16] also found that AgNPs produced through green synthesis using plant extracts usually form spherical particles within a similar size range of 10 to 100 nm, supporting the findings of this study.

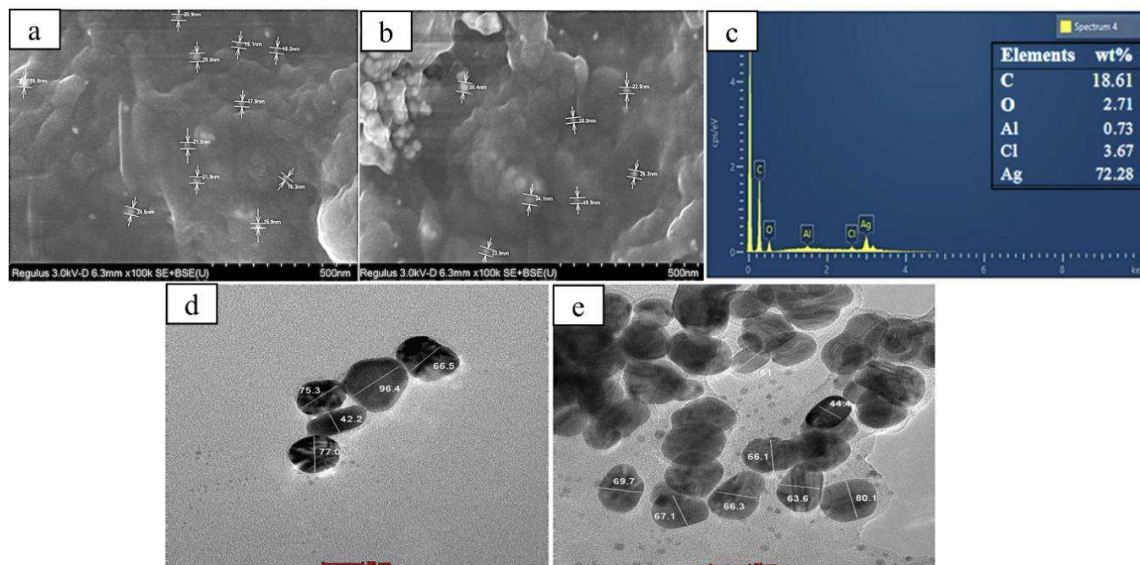


Figure 4: (a) and (b) SEM, (c) EDX, (d) and (e) TEM images of PPT-AgNPs.

3.5. Zetapotential (pH PZC) analysis

Figure 5 shows the pH PZC plot for the PPT-AgNPs. It can be seen that the pH PZC is at 5.77. At this pH value, the surface charge of the AgNPs is zero. However, at a higher pH of 5.77, the surface of the PPT-AgNPs becomes negatively charged, while lower pH values cause the surface to become positively charged.

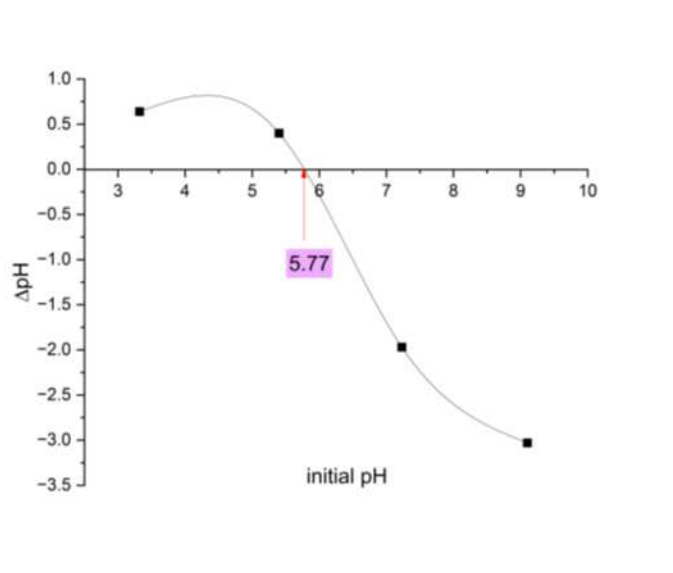


Figure 5: pH PZC plot for PPT-AgNPs

3.6. Photocatalytic Degradation of MB

The UV-Vis absorption spectra shown in **Figure 6(a)** illustrate the photocatalytic degradation of MB over 5 hours using synthesised PPT-AgNPs as a catalyst. The absorption measurements were taken in the range of 500 – 700 nm, focusing on the characteristic peak of MB at 661 nm, which provides important details about its molecular structure and concentration in the solution.

Initially (0 min), the solution shows a strong absorbance peak at 661 nm, which confirms the presence of a high concentration of MB. The peak intensity decreases more steeply in the first hour, indicating a higher degradation rate at the beginning of the reaction. This could be due to the abundance of MB molecules and reactive species, like hydroxyl radicals, produced by UV-excited AgNPs. As the UV irradiation continues, the absorbance at this wavelength gradually decreases. The degradation rate begins to slow, a common pattern in photocatalytic reactions, as the MB concentration decreases and the system approaches equilibrium [40]. This decreasing absorbance trend indicates that the MB chromophore is degrading over time, demonstrating effective photocatalytic activity [41]. By the 5th hour, the absorbance at 661 nm has significantly decreased, suggesting that a large amount of MB has been degraded. The degradation efficiency is 87.37%, confirming the high photocatalytic efficiency of the PPT-AgNPs. This result indicates that the PPT-AgNPs, which were synthesised using tannin as both a reducing and capping agent, effectively catalyze the degradation process under UV light. Furthermore, it has been reported that tannins not only stabilize the nanoparticles but also enhance photocatalytic activity by donating electrons to the conduction band of PPT-AgNPs, thereby promoting the generation of reactive species for MB degradation [42].

A control experiment without PPT-AgNPs showed minimal degradation of MB under UV light, confirming that the observed photodegradation is primarily due to the catalytic action of the PPT-AgNPs. This is shown in **Figure 6(b)**. This finding is consistent with Ekennia et al. [43], who reported that MB degradation was negligible in the absence of AgNPs, but was significantly enhanced when AgNPs synthesized using *Magnolia kobus* extract were introduced under UV irradiation.

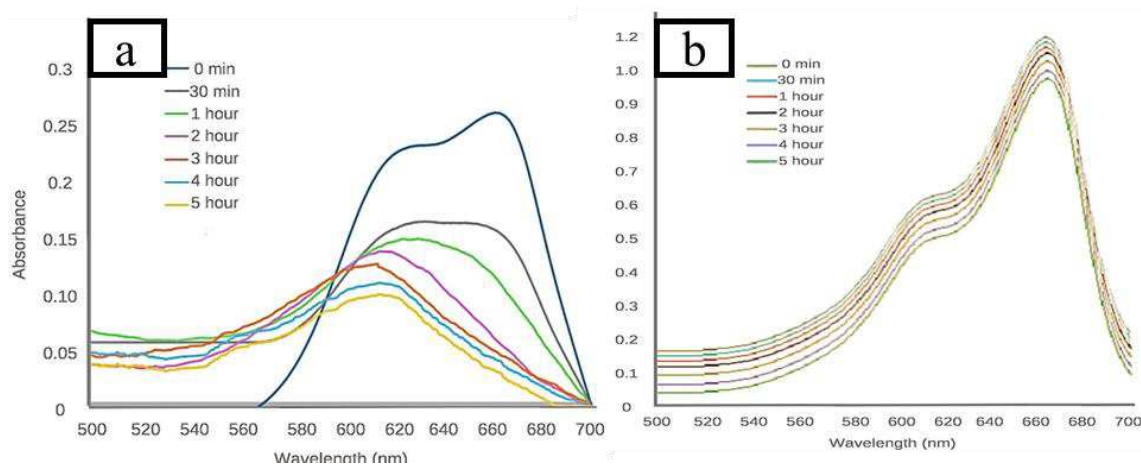


Figure 6: UV-Vis spectra of MB (a) in the presence of and (b) in the absence of PPT-AgNPs over time under UV light.

3.7. Effect of pH on Photocatalytic Degradation Efficiency

The photocatalytic degradation of MB using PPT-AgNPs was evaluated under different pH levels: pH 3, pH 5, pH 8, and pH 9. The goal was to see how acidity or basicity affects degradation performance. The trend in degradation efficiency at various pH levels can be seen in **Figure 7**, where pH 5 shows the highest degradation performance compared to pH 3, 8, and 9. This outcome emphasizes that slightly acidic conditions enhance the photocatalytic activity of PPT-AgNPs relative to basic conditions. Typically, photocatalytic trends are explained based on the structure of the MB and the surface charge of the catalyst, in this case the PPT-AgNPs. However, the observation cannot be explained based on this reasoning as the trend observed can be explained based on the structure of the MB changes with pH. At a pH of more than 6, only 2 of the 3 nitrogens in the MB structure are protonated. In contrast, below pH 5.4 all 3 of the nitrogens are protonated.

This results in the MB structure being more positively charged at a pH lower than 5.4 compared to pH values more than 6. Considering the surface charge of the PPT-AgNPs, electrostatic repulsion should occur at pH values below 5.4, while electrostatic attraction should be more dominant at pH values above 6, resulting in better activity at higher pH values. As this trend was not observed in this work, it can only be summarized that other factors played a more critical role in influencing the photodegradation of the MB at different pH values. The lower photodegradation percentage observed at pH 3 compared to pH 5 may be due to the dissolution of AgNPs to form Ag^+ ions in very acidic conditions. In contrast, the lower catalytic activities

observed at pH 8 and 9, may be attributed to the change in the structure and stability of tannin, which can undergo deprotonation at higher pH values.

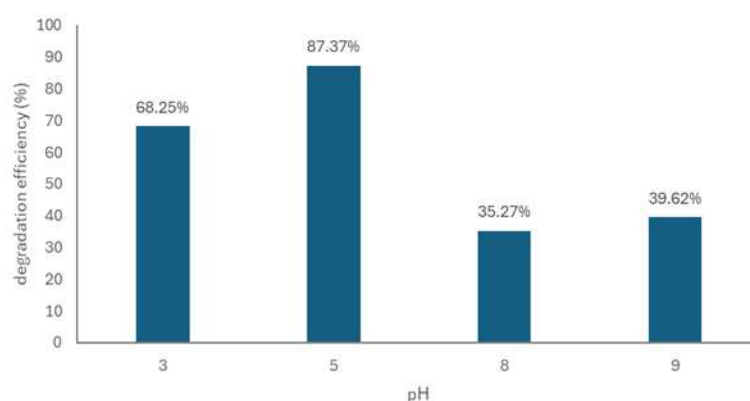


Figure 7: The percentage degradation efficiency in photocatalytic degradation of MB at different pH levels after 5 hours.

3.8. Effect of Scavenger on Photocatalytic Degradation Efficiency

To explore the role of reactive species in the photocatalytic degradation mechanism, 0.1 M of various scavengers were used: EDTA for photogenerated holes (h^+), ascorbic acid for superoxide radical ($\bullet O_2^-$), and isopropanol for hydroxyl radical ($\bullet OH$). As shown in **Figure 8a**, the degradation efficiency dropped from 87.37% (no scavenger) to 49.28% when EDTA was added, indicating that h^+ played a smaller role in MB degradation. This could be attributed to direct oxidation by h^+ or enhanced electron-hole separation when holes are scavenged [44]. Meanwhile, with ascorbic acid, the catalytic degradation dropped to 41.67%, suggesting that $\bullet O_2^-$ also contributes to photodegradation, however, playing a slightly more significant role when compared to h^+ . Conversely, the addition of isopropanol caused the degradation to decrease the most, resulting in only 32.43% catalytic degradation. This implies that $\bullet OH$ played a major role in this system. The reduction in efficiency caused by each scavenger highlights the relative importance of each reactive species in the photocatalytic process.

Figure 8b illustrates the photocatalytic degradation mechanism of MB using synthesized PPT-AgNPs under UV light exposure. Upon exposure to light, the PPT-AgNPs absorb photons, which helps move electrons (e^-) from the valence band (VB) to the conduction band (CB), creating h^+ in the VB [45]. Subsequently, these charge carriers initiate redox reactions that produce reactive oxygen species (ROS), which play a key role in MB degradation[46]. Specifically, the electrons in the conduction band reduce molecular oxygen (O_2) into $\bullet O_2^-$,

which can then react to form hydrogen peroxide (H_2O_2) and eventually $\bullet\text{OH}$ [47]. Simultaneously, the H^+ in the valence band oxidize water (H_2O) to create even more $\bullet\text{OH}$ radicals [48]. Consequently, these ROS, especially $\bullet\text{O}_2^-$ and $\bullet\text{OH}$, along with direct oxidation by h^+ , degrade MB into carbon dioxide (CO_2) and water (H_2O) [46].

Finally, the findings align well with previous studies, including those by Zhang et al. [49], who reported that natural polyphenols, such as tannins, not only help stabilize AgNPs but also enhance light absorption and facilitate effective ROS generation. In summary, this mechanism highlights the synergistic effect of PPT-AgNPs and emphasizes the crucial roles of holes and superoxide radicals in MB degradation.

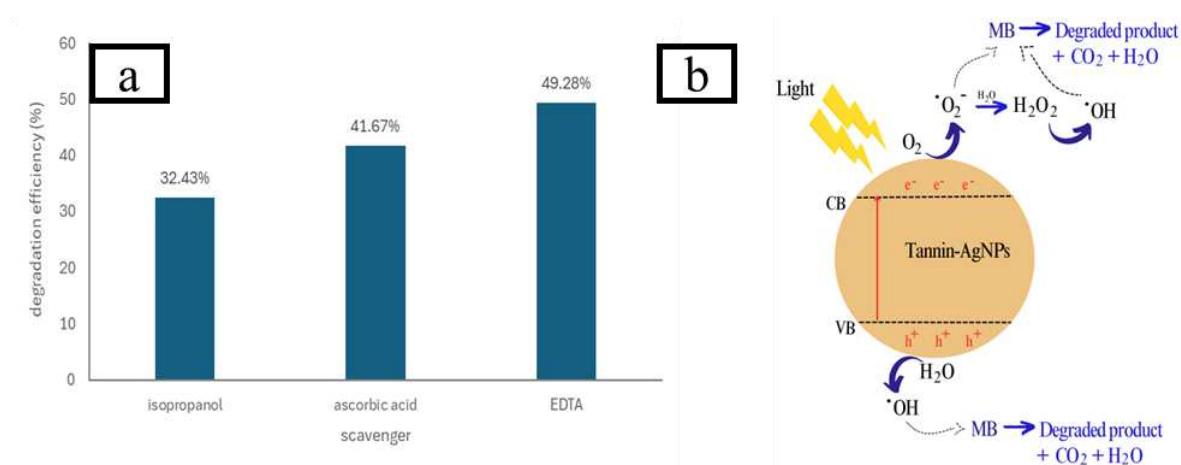


Figure 8: (a) The percentage degradation efficiency in photocatalytic degradation of MB for each scavenger after 5 hours, and (b) photocatalytic degradation mechanism of MB over PPT-AgNPs.

3.9. Effect of Temperature on Photocatalytic Degradation Efficiency

The effect of temperature on the photocatalytic degradation of MB was investigated at the following five different temperatures: 20°C , 25°C , 30°C , 35°C , and 40°C , over a reaction period of 5 hours. The results are displayed in two forms: **Figure 9a** shows a line graph illustrating the degradation efficiency over time for each temperature, while **Figure 9b** presents a bar chart comparing the final degradation efficiencies at each temperature after 5 hours.

From the time-based degradation efficiency graph (**Figure 9a**), it is evident that temperature plays a crucial role in the rate and effectiveness of photocatalytic degradation. Among all the tested conditions, 30°C showed the highest degradation efficiency, reaching over 85%

after 5 hours. This indicates that 30°C provides the most favourable environment for photocatalytic activity, likely because it optimally activates the photocatalyst and enhances the production of reactive species such as $\bullet\text{OH}$ [50]. At 25°C, degradation efficiency also increased rapidly over the first two hours and plateaued at around 63%, indicating moderately effective photocatalytic performance. In contrast, at 20°C, the reaction was noticeably slower and less effective, only reaching about 47.51% efficiency by the fifth hour. This slower pace can be attributed to reduced molecular motion and a slower formation of reactive species at lower temperatures, which limits the overall photocatalytic performance [51]. Interestingly, when temperatures rose above the optimal 30°C, degradation efficiency dropped at 35°C and 40°C. While 35°C showed a moderate performance of about 60.68%, 40°C had a lower final efficiency of around 51.73%, which is only slightly better than what was observed at 20°C. This decline can be attributed to potential thermal deactivation of the photocatalyst at higher temperatures, along with increased desorption of dye molecules from the catalyst surface, reduced oxygen solubility, or even thermal decomposition of the catalyst involved in the degradation process [52].

These trends are clearly illustrated by the bar graph (**Figure 9b**), which provides a summary of the final degradation efficiencies. It shows a noticeable increase in efficiency as the temperature rises from 20°C to a peak at 30°C before decreasing at higher temperatures. This non-linear trend emphasizes that while increasing temperature can initially enhance photocatalytic performance, surpassing the optimal range can negatively impact the reaction. In brief, 30°C is the optimum for achieving maximum efficiency. Temperatures that are too low or too high can reduce effectiveness, highlighting the importance of thermal optimization in practical applications.

In addition to degradation efficiency, further insight into the temperature effect on photocatalytic degradation can be obtained by analyzing the rate constant values. These values were derived from the slopes of the linear plots of $\ln(C_0/C)$ against time, which are presented in **Figure 9c**. The trend in the rate constants reflects the degradation efficiency discussed earlier. Specifically, the rate constant ($k = 0.4961 \text{ hour}^{-1}$) reaches its highest point at 30°C, which corresponds to the highest degradation efficiency of over 85%. At 25°C, the reaction proceeds quite well ($k = 0.2972 \text{ hour}^{-1}$), but when the temperature drops to 20°C, the lowest rate constant was recorded ($k = 0.0959 \text{ hour}^{-1}$). Interestingly, the rate constants start to drop again at 35°C and 40°C, where $k = 0.2316 \text{ hour}^{-1}$ and $k = 0.1797 \text{ hour}^{-1}$, respectively. This implies that even

though the temperatures are higher, photocatalytic performance is hindered, likely due to thermal deactivation or unfavorable changes in surface adsorption dynamics [52].

Generally, the rate constants increased from 20°C to 30°C, indicating enhanced photocatalytic activity due to improved mass transfer, adsorption kinetics, and charge carrier mobility. However, a decline in k was observed at 35°C and 40°C, suggesting the onset of competing effects. At higher temperatures, the adsorption of MB onto the PPT-AgNPs surface is likely weakened due to the exothermic nature of adsorption, resulting in reduced surface coverage. Additionally, increased thermal energy may accelerate electron–hole recombination, thereby decreasing the availability of reactive species. Hence, the non-monotonic behavior observed, indicates that the system deviates from classical Arrhenius kinetics and is governed by a balance between kinetic enhancement and surface or recombination limitations. Consequently, 30°C represents an optimal condition where these competing factors are balanced to maximize degradation efficiency.

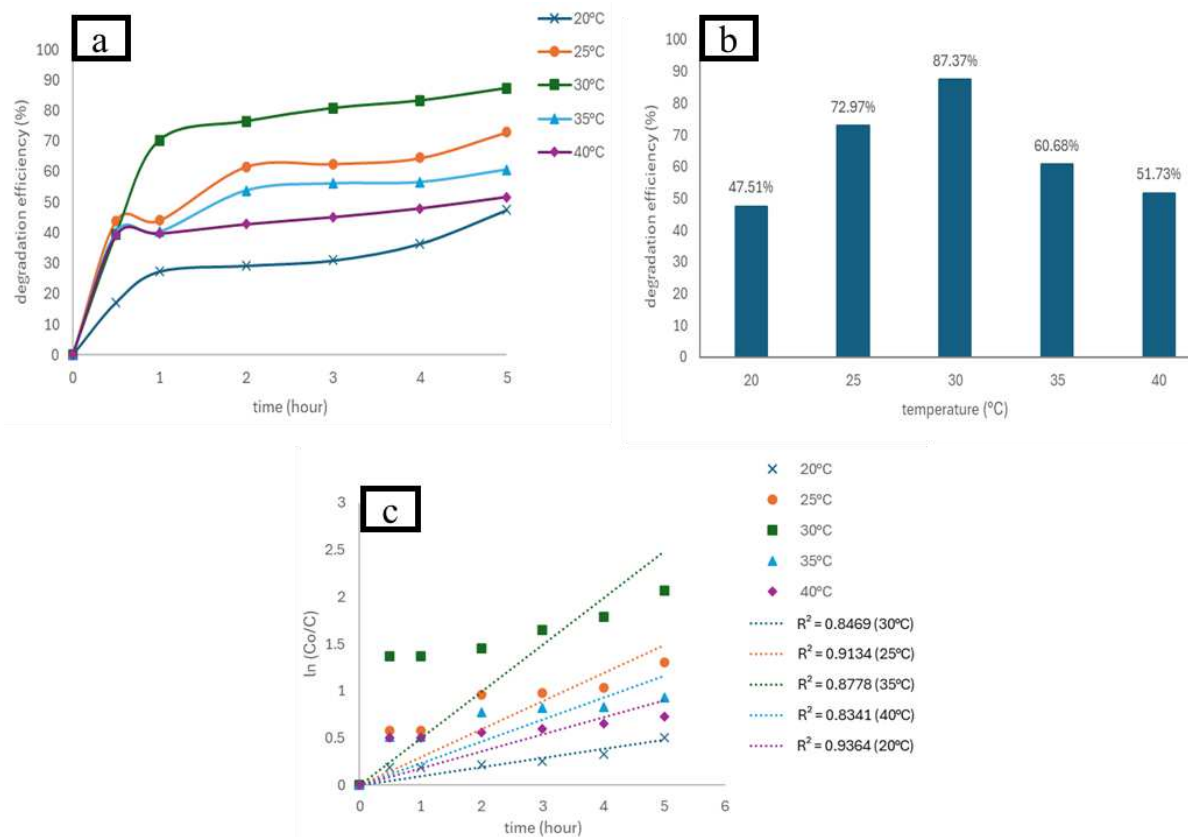


Figure 9: (a) Percentage degradation efficiency of methylene blue (MB) during photocatalytic degradation over 5 h at different temperatures; (b) Percentage degradation efficiency of MB after 5 h of photocatalytic reaction at different temperatures and (c) Pseudo-first-order kinetic plots of $\ln(C_0/C)$ versus time at different temperatures.

4. Conclusion

In conclusion, this study successfully synthesized PPT-AgNPs using AgNO₃ and *Pinus pinaster*'s tannin through a green synthesis. The synthesized PPT-AgNPs exhibited particle sizes ranging from 15.9 to 96.4 nm, confirming their nanoscale dimensions. The concentration of *Pinus pinaster*'s tannin was optimized at 1000 ppm, which enabled the efficient reduction of AgNO₃ into AgNPs. The primary objective of this work was to evaluate the photocatalytic performance of the PPT-AgNPs for the degradation of MB. Optimum photocatalytic conditions were achieved at pH 5 and 30 °C, yielding a degradation efficiency of 87.37% within 5 h. Kinetic analysis revealed that the degradation process followed pseudo-first-order kinetics with a rate constant of 0.4961 h⁻¹. Overall, the successful green synthesis of PPT-AgNPs and their promising photocatalytic performance provide a sustainable approach for dye removal and offer valuable potential for future nanotechnology-based wastewater treatment applications.

CRedit authorship contribution statement

Nur Asyikin Abu Bakar: Data curation, Formal analysis, & Visualization, **Nur Aida AD Sham:** Data curation, Formal analysis, & Visualization, **Nur Najwa Abdul Talib:** Data curation, Formal analysis, Writing – original draft, Methodology. **Noor Hana Hanif Abu Bakar:** Funding acquisition, Supervision, Project administration, Resources, Writing – review & editing. **Pandian Bothi Raja:** Funding acquisition, Project administration, Resources, Writing – review & editing. **Isabelle Ziegler-Devin:** Methodology, Formal analysis, **Nicolas Brosse:** Methodology, Formal analysis, **Arumugam Thangamani:** Manuscript Drafting, **Mohd. Hazwan Hussin:** Methodology, Formal analysis, **Mohamad Nasir Mohamad Ibrahim:** Methodology, Formal analysis.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials. Raw data that support the findings of this study are available upon request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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