

Original Research

Photocatalytic and Catalytic Methods for Organic Azo Dyes and Paranitrophenol Pollutants Removal Using Green Synthesised *Flacourtia indica* Silver Nanoparticles

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Abstract

The advancement of photocatalytic nanomaterials has become central to addressing the growing challenge of removing organic pollutants from water systems through sustainable and efficient degradation pathways. In this study, silver nanoparticles were synthesized via a green approach using aqueous extracts derived from five parts of *Flacourtia indica*, including bark, flower, fruit, seed, and leaves, at 90°C for 45 minutes. UV-VIS spectroscopy (460 nm) confirmed nanoparticle formation, while scanning electron microscope analysis revealed predominantly spherical AgNP with diameters of 50 nm - 70 nm and semiconductor-like band-gap energy. This eco-friendly, non-toxic, and cost-effective synthesis avoided the use of harmful reducing agents. The synthesized silver nanoparticles were evaluated for their photocatalytic performance against organic dyes, catalytic reduction of p-nitrophenol, and cytotoxicity. The photocatalytic efficiency was tested against two organic pollutant dyes, Methylene Blue and Congo Red, under sunlight irradiation and in the presence of sodium borohydride. The 266.67 ppm silver nanoparticles achieved faster degradation of Methylene Blue under sunlight alone, whereas both 4000 ppm and 266.67 ppm silver nanoparticles



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showed enhanced Congo Red degradation under combined sunlight and sodium borohydride conditions. Degradation of para-nitrophenol was investigated in the presence of 266.7 ppm silver nanoparticles, with the Bark_AgNP exhibiting immediate degradation upon sodium borohydride addition. Cytotoxicity evaluation using *Artemia salina* revealed 100% viability at both 800 ppm and 200 ppm AgNP concentrations, indicating their biosafety and potential environmental compatibility. Overall, these results demonstrate that green-synthesized *F. indica*-based silver nanoparticles possess efficient photocatalytic and non-toxic characteristics, making them promising candidates for sustainable environmental remediation applications.

Keywords

Flacourtia indica; silver nanoparticles; photocatalytic degradation; organic pollutant removal; catalytic reduction; para-nitrophenol reduction; methylene blue; Congo red; environmental remediation; cytotoxicity

1. Introduction

The rapid advancement of nanotechnology has introduced new pathways for developing materials with exceptional physicochemical and catalytic properties at the nanoscale (1-100 nm). Among these materials, silver nanoparticles (AgNPs) have garnered significant attention due to their remarkable optical, antimicrobial, and catalytic behaviours, which arise from their high surface area-to-volume ratio and enhanced surface [1, 2]. In recent years, AgNPs have been extensively studied as catalytic and photocatalytic materials for environmental remediation, where they play a vital role in the degradation and reduction of organic pollutants such as dyes and phenolic compounds [3].

AgNPs are synthesised through two foundational approaches: the bottom-up approach, which builds nanoparticles from atomic precursors through chemical or biological processes, and the top-down approach, which breaks down bulk materials into nanoscale particles using physical or mechanical methods [4]. Depending on the size and size distribution control required, the synthesis approach, along with the agents used, can be changed. However, conventional physical and chemical methods used for synthesising AgNPs often rely on toxic reducing agents, organic solvents, and energy-intensive processes, which limit their environmental compatibility [5, 6]. To address these drawbacks, green synthesis has emerged as an efficient, sustainable, and eco-friendly alternative. This approach utilises biological systems such as plants, algae, fungi, and microorganisms as natural sources of reducing and stabilising agents [7]. Among them, plant-mediated synthesis is particularly favoured because it is simple, cost-effective, and free from pathogenic contamination while providing abundant phytochemicals that not only facilitate the reduction of silver ions (Ag^+) to elemental silver (Ag^0) but also stabilise the resulting nanoparticles with a capping agent, preventing aggregation and enhancing their bioactivity [8, 9]. Additionally, plant-based research ensures that biodegradable plant components are used. This promotes the use of naturally available plant material for the production of sustainable nanoparticles, which in turn lessens the impact on the environment through safe disposal and the ability to incorporate the nanoparticles in industrial applications without impacting health and the environment [10].

Within this framework, *Flacourtia indica* (*F. indica*) (Governor's Plum) represents a promising biological resource for green nanotechnology. It is a tropical plant widely distributed across Asia and Africa and is traditionally valued for its medicinal and antioxidant properties [11]. Various parts of *F. indica*, like the fruit, bark, leaves, and roots, are known for medical applications, such as in the treatment of vomiting, fever, inflammation, and jaundice. The existing research has circulated around the phytochemical profiling of *F. indica* parts under different extraction methods to contain secondary metabolites such as phenolics, flavonoids, tannins, terpenoids, and proteins. These compounds are responsible for the wide range of activities exhibited by *F. indica*, such as antioxidant, anticancer, antiproliferative, antidiabetic, and anti-obesity [12, 13]. Furthermore, few studies on *F. indica* AgNPs have been conducted, which have shown successful synthesis, anticancer potential against cancer cell lines, antibacterial activity, and anti-proliferative activity [14]. These secondary metabolites or phytochemical compounds not only provide therapeutic benefits but also supply natural functional groups capable of reducing metal ions and stabilising nanoparticles. The biochemical diversity of the plant makes it a multifunctional biological matrix for nanoparticle synthesis, offering different phytochemical environments that can influence nanoparticle formation, morphology, and catalytic activity [14].

Due to these attributes, *F. indica* has been utilised for the green synthesis of AgNPs, aimed at enhancing their potential environmental applications, particularly in photocatalysis and p-nitrophenol (PNP) catalysis [15]. Industrial organic pollutants such as Methylene Blue (MB), Congo Red (CR), and PNP are not only toxic and carcinogenic but also resistant to conventional degradation methods such as photolysis, biodegradation, and chemical oxidation. These compounds are commonly released into aquatic environments through effluents from textile, dyeing, paper, pharmaceutical, and agrochemical industries. Their persistent chemical stability and slow biodegradability lead to accumulation in water bodies, disrupting aquatic ecosystems and posing long-term risks to human health [16, 17]. AgNPs, with their strong surface plasmon resonance (SPR) and electron transfer abilities, serve as effective catalysts for transforming these toxic pollutants into less harmful products under light or chemical reduction conditions [3]. Due to these benefits, AgNPs synthesised from various plant species have been investigated for industrial usage, utilising wastewater to observe changes in water quality parameters following the addition of AgNPs. These research findings further support the idea that plant-mediated AgNPs could be used as a wastewater remediator [18-20].

Importantly, the phytochemical composition and concentration vary significantly among different plant parts, leading to distinct reducing and capping environments during nanoparticle synthesis [21, 22]. This variability forms the scientific basis for employing multiple parts of *F. indica*, with the hypothesis that phytochemical diversity directly governs AgNP nucleation, growth kinetics, surface chemistry, and catalytic performance. A systematic comparison of AgNPs synthesized from different plant parts, therefore, enables elucidation of structure-property-function relationships [23].

Along with finding a suitable green alternative to address environmental remediation, the safety and biocompatibility of the synthesised nanoparticles are equally important. Bioassays such as the *Artemia salina* (*A. salina*) (brine shrimp) lethality test provide a simple and reliable method for evaluating nanoparticle cytotoxicity, offering insights into their potential environmental and biological impact [24, 25]. Exposure to toxic AgNPs leads to interaction with cellular components, resulting in the generation of reactive oxygen species (ROS), which can cause oxidative damage. The

larvae's transparent exoskeleton makes it easy for direct observation of survival rates and mobility, making *A. salina* an efficient model for assessing both acute and chronic toxicity in biomedical and environmental research [26]. It is acknowledged that the *A. salina* assay represents a preliminary toxicity screening model giving rapid results. However, comprehensive evaluation of long-term environmental impact requires further ecotoxicological studies involving aquatic plants and microbial communities [27, 28]. In addition to pollutant degradation, AgNPs have attracted increasing interest in water disinfection applications due to their broad-spectrum antimicrobial activity against pathogenic and multidrug-resistant bacteria [29]. Green-synthesised AgNPs, particularly when stabilised by phytochemical capping agents, offer potential for integrated water treatment strategies combining catalytic pollutant removal and microbial inactivation while minimising uncontrolled silver ion release [30]. In this study, the cytotoxicity of *F. indica* AgNPs using *A. salina* will address the gap in systematic cytotoxicity data for the target AgNPs and clarify their biosafety profile for environmental applications.

Hence, the present study focuses on the green synthesis of AgNPs using different parts of *F. indica* and their evaluation as catalysts in the photocatalytic degradation of dyes (MB and CR) and the catalytic reduction of PNP. Additionally, the cytotoxic properties of the synthesised AgNPs are assessed to ensure environmental safety. The morphological characteristics of the nanoparticles are examined using a scanning electron microscope (SEM) to establish the relationship between synthesis conditions, structure, and catalytic performance. Unlike previous studies that relied on single plant parts or limited catalytic evaluation, this work presents a comprehensive, multi-part comparative analysis of *F. indica*-derived AgNPs, integrating physicochemical characterisation, photocatalytic dye degradation, catalytic PNP reduction, and cytotoxicity assessment. This approach highlights the novelty of correlating plant-part-specific phytochemistry with nanoparticle functionality, thereby advancing eco-friendly nanocatalyst design for water treatment applications.

2. Materials and Methods

2.1 Sample Collection

Multiple parts of *F. indica* were collected from home gardens in Ratmalana and Beruwala, Sri Lanka (Figure 1).

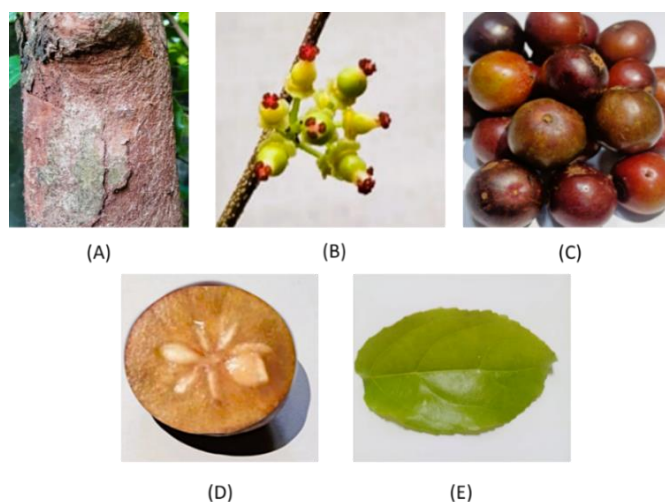


Figure 1 Five *F. indica* parts used, A - Bark, B - Flower, C - Fruit, D - Seed and E - Leaves.

2.2 Preparation of Extracts

The collected samples were carefully wiped with a soft cloth and air-dried for five days. A mixture of 2 g of samples that were ground using a mortar and pestle, and 50 mL of distilled water (DW) was added. The mixture was boiled at 100°C for 15 minutes. After heating, samples were cooled, filtered through Whatman No.1 filter paper to obtain the water extracts (WE), and stored at 4°C for analysis [31].

2.3 Synthesis of AgNP and Optimization

The AgNP synthesis occurred at different temperatures and time intervals; 1 mL of WE was mixed with 9 mL of 1 mM Silver Nitrate (AgNO₃). The mixtures were incubated at 90°C and 60°C for 15, 30, 45, and 60 minutes in a dry oven and in a dark environment at room temperature (RT) for 24 hours. The color transformation was observed before and after the optimization, and the absorbance was measured from 320 nm to 520 nm, using DW as a blank [32].

2.4 SEM Analysis

Bark_AgNP was centrifuged at 10,000 rpm for 2 minutes and repeated until the pellet was formed, which was oven-dried at 40°C for 24 hours and outsourced to SLINTEC, Sri Lanka, for the SEM analysis.

2.5 Photocatalytic Activity of AgNP Using MB and CR Dye

Initially, the absorbance spectrum for a 1 mM MB solution was obtained by recording the absorbance from 380 nm to 780 nm. Photocatalytic activity was tested with and without a catalyst; (1) 50 mL of 1 mM MB was mixed with 0.5 mL of 4000 ppm or 266.7 ppm AgNPs and exposed to sunlight, (2) 50 mL of 1 mM MB was mixed with 0.5 mL of 4000 ppm or 266.7 ppm AgNPs and 1 mL of 0.2 M NaBH₄. The absorbance from 380 nm to 780 nm was recorded every 30 minutes for 120 minutes using DW as the blank. This experiment design was replicated for CR under the same conditions [32].

2.6 PNP Catalysis Activity of AgNP

The absorbance of 0.1 mM of PNP was obtained for the wavelength range of 280 nm to 520 nm. Next, the absorbance of 1 mL of 0.1 M NaBH₄ with 2 mL of 0.1 mM of PNP was obtained. Then, the absorbance of 20 µL of 266.67 ppm AgNPs with 1 mL of 0.1 M NaBH₄ and 2 mL of 0.1 mM of PNP was taken every 10 minutes. All absorbance was taken using DW as a blank [33].

2.7 Cytotoxicity Assay of AgNPs

A. salina cysts were incubated in seawater under yellow light with aeration for 24 hours. Two test concentrations of AgNPs (800 ppm and 200 ppm) were prepared by mixing 50 µL of the 800 ppm and 12.5 µL of the 200 ppm with 200 µL and 237.5 µL of seawater, respectively, in individual wells of a 96-well plate. Each well received two *A. salina* larvae, and seawater containing larvae without AgNPs served as the positive control. Plates were incubated for another 24 hours in triplicate, and percentage viability was calculated using equation (1) [34].

$$\text{Percentage viability} = \frac{\text{Total no of viable shrimps} - \text{Total no of non-viable shrimps}}{\text{Total no of viable shrimps}} \times 100 \quad (1)$$

3. Results

3.1 Synthesis of *F. indica* AgNP and Optimization

Reduction of silver ions to silver was observed in the samples through colour change from pale yellow to brownish yellow (Figure 2). The synthesis of *F. indica* plant parts was not obtained at 60°C and RT. Among the synthesized conditions, the ideal temperature and time duration are confirmed as 90°C for 45 minutes (Table 1). The successful synthesis at 90°C for 45 minutes is confirmed by AgNP peaks at 460 nm (Figure 3).

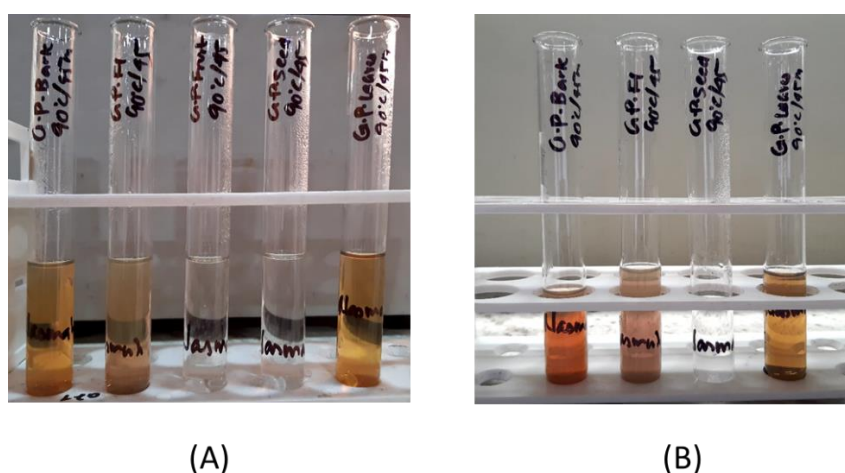


Figure 2 A distinctive color shift from pale yellow before incubation with WE and silver nitrate solution before heating (A) to brownish yellow after incubation (B), confirming the formation of silver nanoparticles.

Table 1 Optimization of *F. indica* plant AgNPs at 60, 90°C, and RT ([v] indicates as synthesized; [x] indicates as not synthesized).

Sample ID	90°C				60°C				R.T/24 h
	15 min	30 min	45 min	60 min	15 min	30 min	45 min	60 min	
Bark	[v]	[v]	[v]	[v]	[x]	[x]	[x]	[x]	[x]
Flower	[x]	[v]	[v]	[x]	[x]	[x]	[x]	[x]	[x]
Fruit	[x]	[x]	[x]	[x]	[x]	[x]	[x]	[x]	[x]
Seed	[x]	[x]	[v]	[x]	[x]	[x]	[x]	[x]	[x]
Leaves	[v]	[v]	[v]	[v]	[x]	[x]	[x]	[x]	[x]

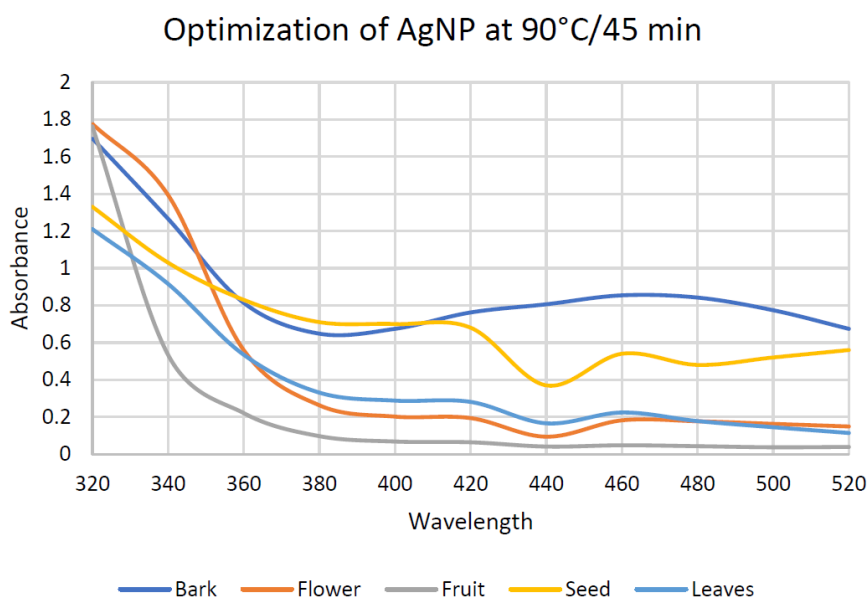


Figure 3 UV-visible spectrum of *F. indica* plant AgNPs synthesized at an optimized condition of 90°C for 45 minutes.

3.2 SEM Analysis of AgNP

The SEM analysis of Bark_AgNP confirmed the presence of AgNPs in spherical shapes with a size range of 50 nm to 70 nm (Figure 4).

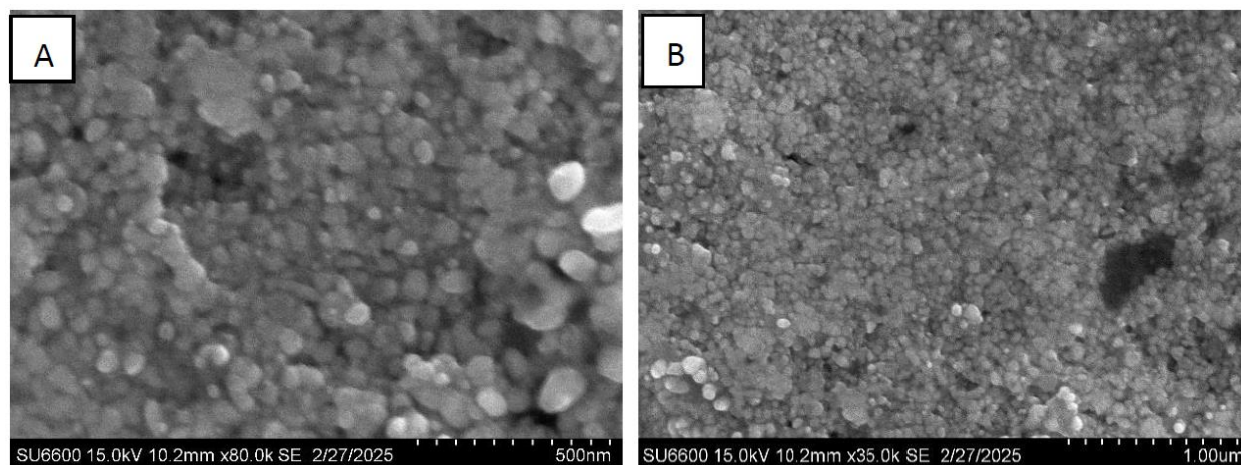


Figure 4 Micrographs of Bark_AgNP SEM analysis. (A) 15.0 kV 10.2 mm × 80.0 k. 500 nm. (B) 15.0 kV 10.2 mm × 35.0 k. 1 μm.

3.3 Photocatalytic Activity of AgNP

3.3.1 Photocatalytic Activity of AgNP for MB

The MB dye peak is observed at 660 nm (Figure 5), which should decrease, indicating the successful degradation of MB dye. The experiments conducted with the *F. indica* AgNPs under sunlight did not show significant MB degradation, with 4000 ppm samples showing faster degradation potential. However, the addition of NaBH₄ accelerated MB reduction (Figures 6-9).

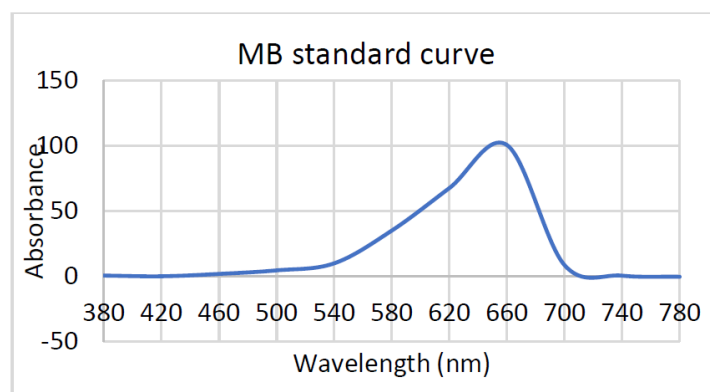


Figure 5 Absorbance spectrum of MB.

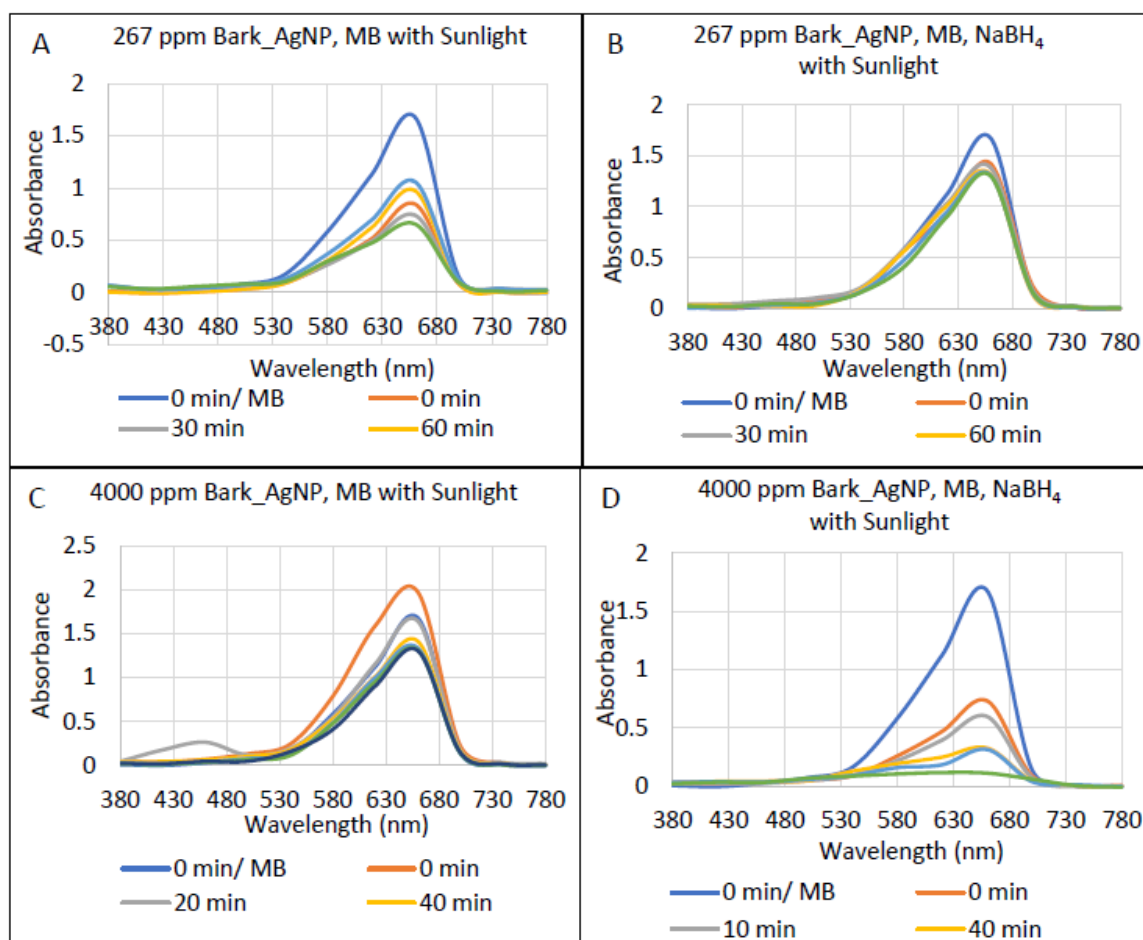


Figure 6 Photocatalytic activity of Bark_AgNP for MB; A - 266.7 ppm Bark_AgNP under sunlight, B - 266.7 ppm Bark_AgNP with NaBH₄ under sunlight, C - 4000 ppm Bark_AgNP under sunlight, and D - 4000 ppm Bark_AgNP with NaBH₄ under sunlight.

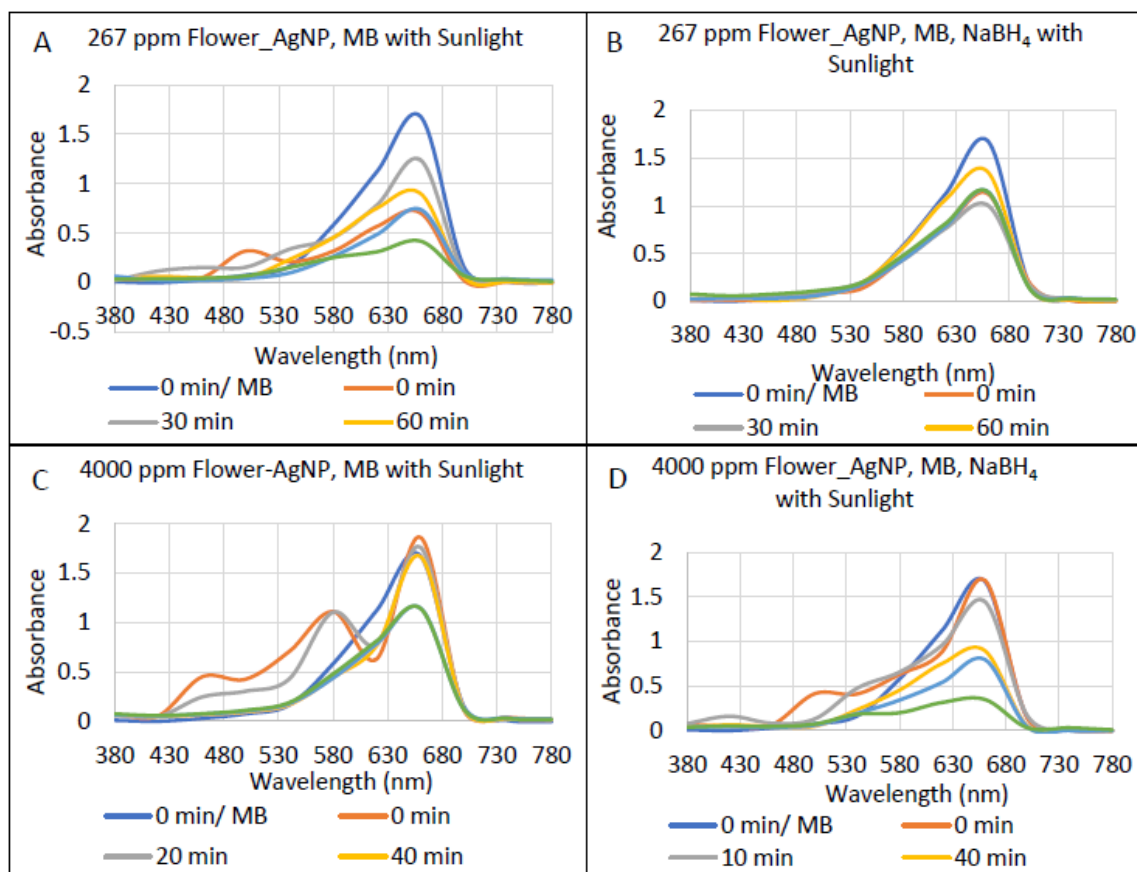


Figure 7 Photocatalytic activity of Flower_AgNP for MB; A - 266.7 ppm Flower_AgNP under sunlight, B - 266.7 ppm Flower_AgNP with NaBH₄ under sunlight, C - 4000 ppm Flower_AgNP under sunlight, and D - 4000 ppm Flower_AgNP with NaBH₄ under sunlight.

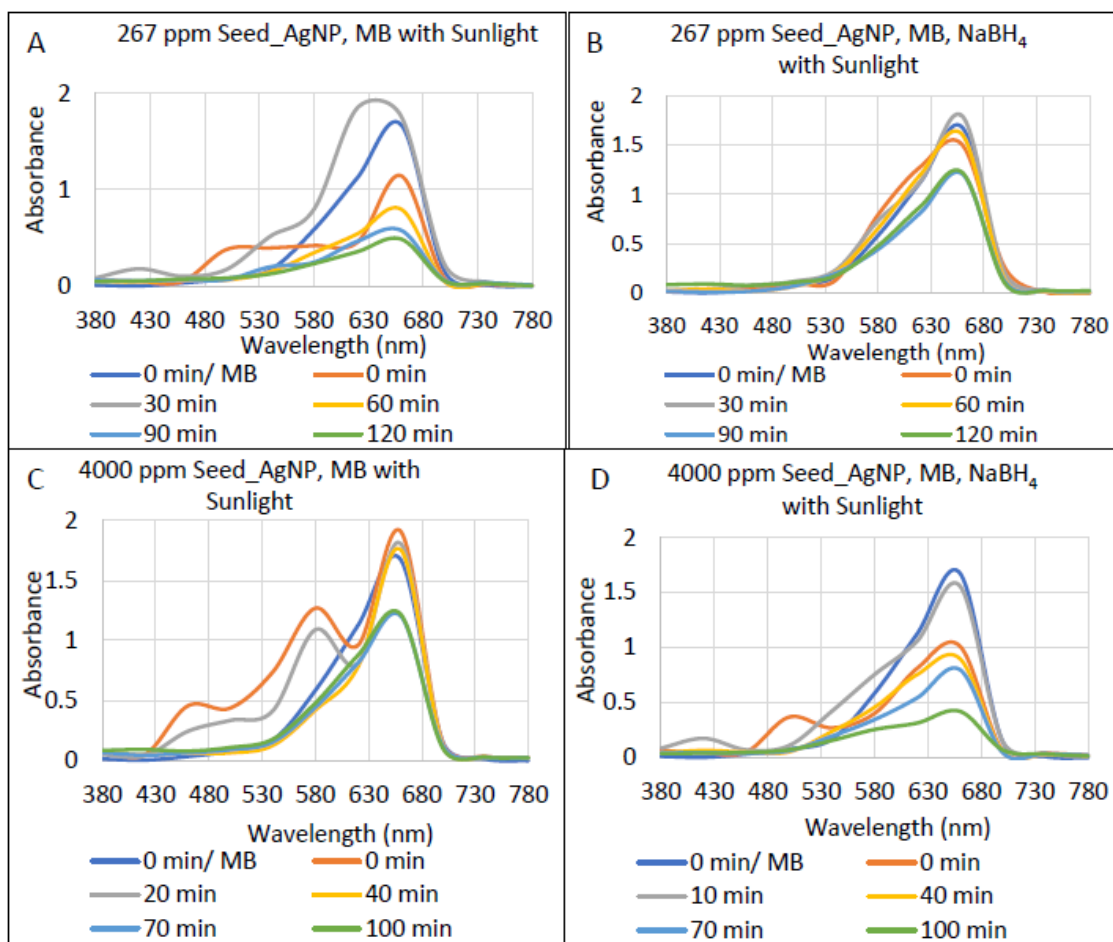


Figure 8 Photocatalytic activity of Seed_AgNP for MB; A - 266.7 ppm Seed_AgNP under sunlight, B - 266.7 ppm Seed_AgNP with NaBH₄ under sunlight, C - 4000 ppm Seed_AgNP under sunlight, and D - 4000 ppm Seed_AgNP with NaBH₄ under sunlight.

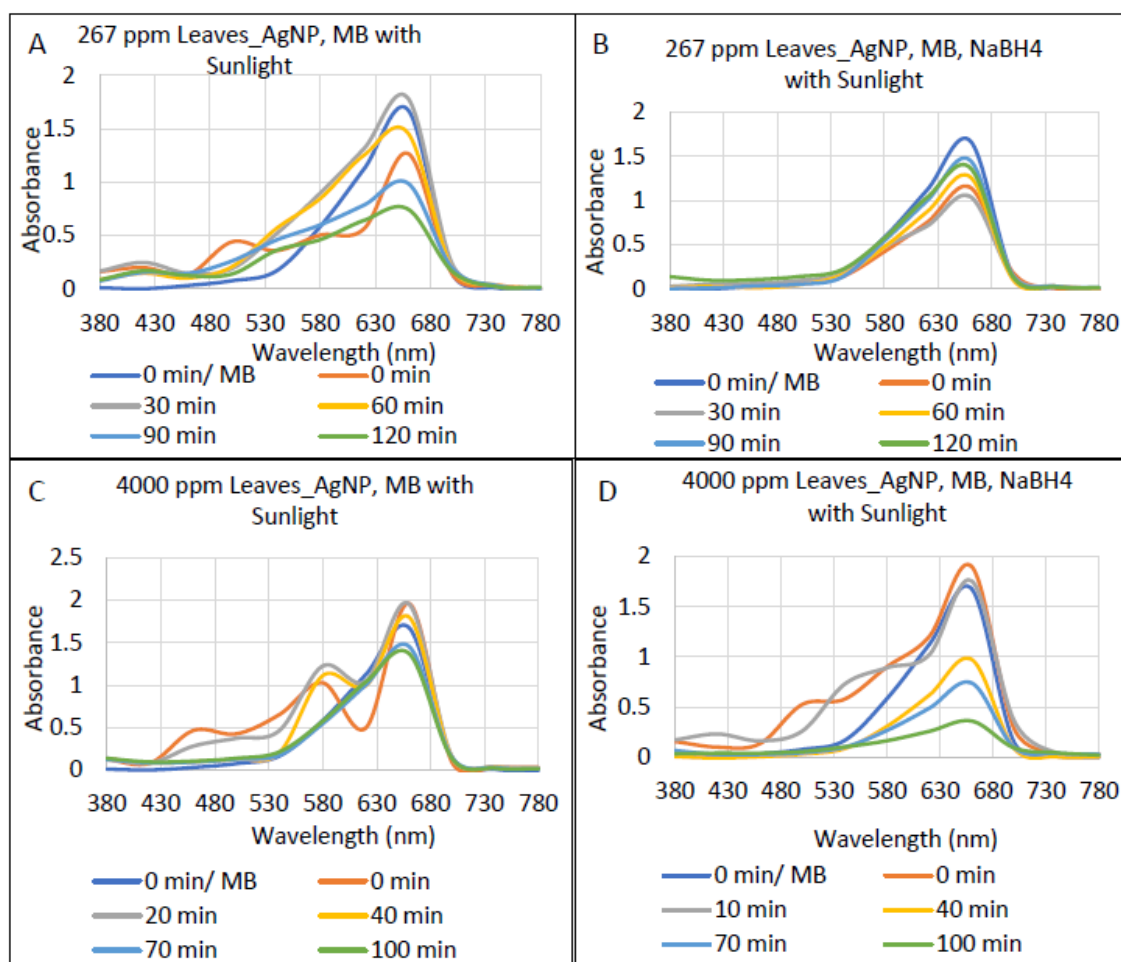


Figure 9 Photocatalytic activity of Leaves_AgNP for MB; A - 266.7 ppm Leaves_AgNP under sunlight, B - 266.7 ppm Leaves_AgNP with NaBH₄ under sunlight, C - 4000 ppm Leaves_AgNP under sunlight, and D - 4000 ppm Leaves_AgNP with NaBH₄ under sunlight.

3.3.2 Photocatalytic Activity of AgNP for CR

The CR dye peak is observed at 500 nm (Figure 10), which should decrease, indicating the successful degradation of the CR dye. Similar degradation patterns with CR dye are observed; 4000 ppm AgNPs have shown faster degradation compared to 266.7 ppm AgNPs, and the addition of NaBH₄ accelerated CR reduction (Figures 11-14).

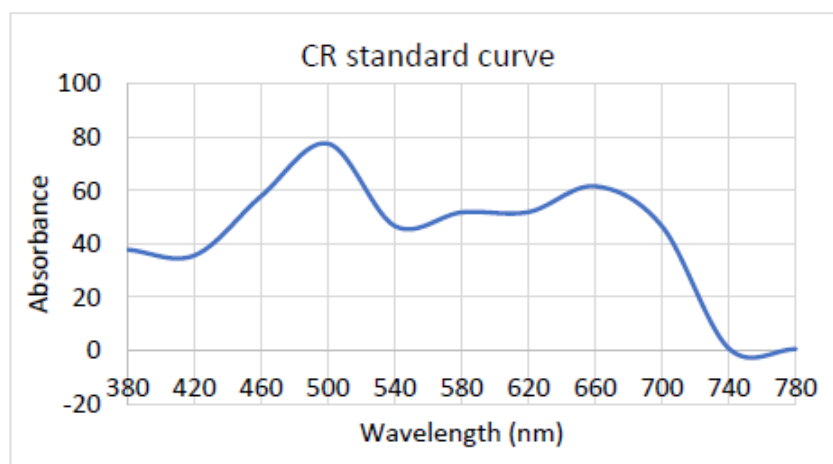


Figure 10 Absorbance spectrum of CR.

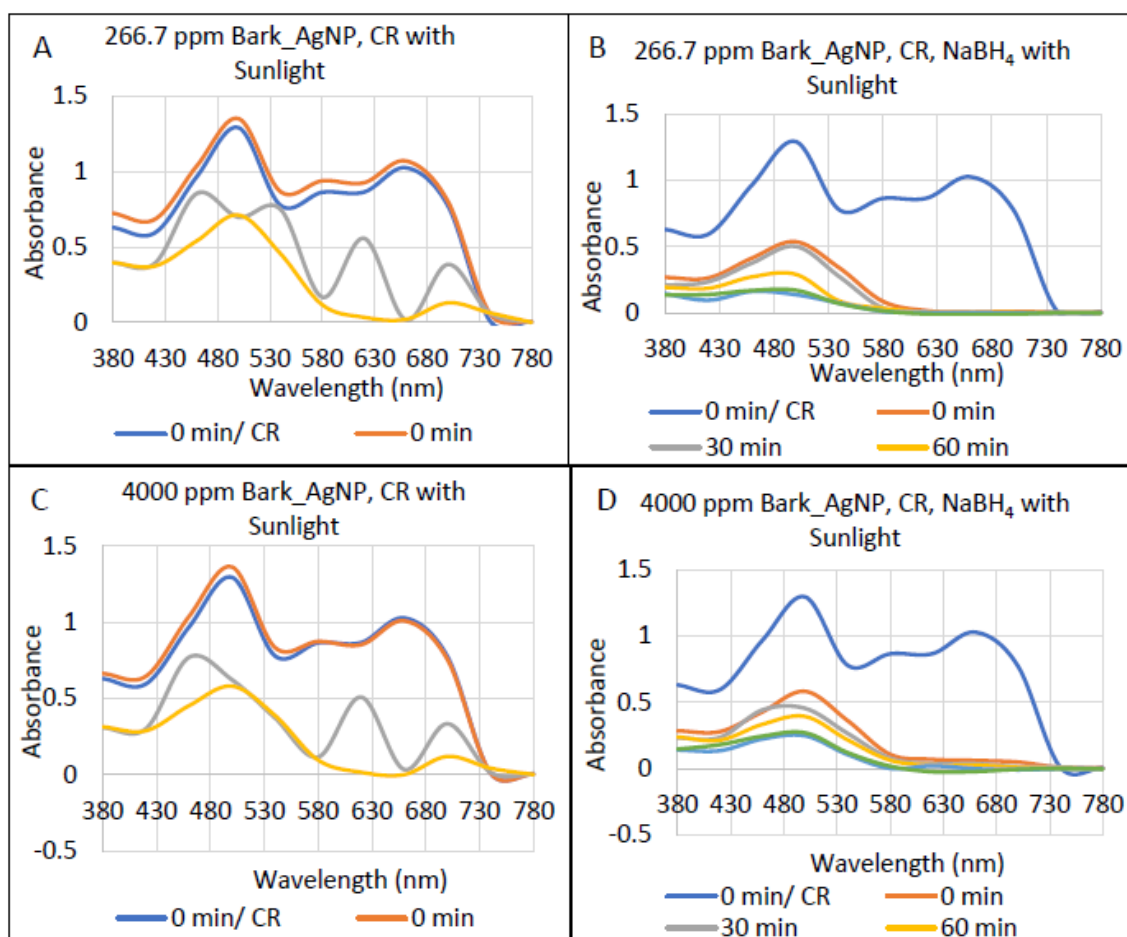


Figure 11 Photocatalytic activity of Bark_AgNP for CR; A - 266.7 ppm Bark_AgNP under sunlight, B - 266.7 ppm Bark_AgNP with NaBH₄ under sunlight, C - 4000 ppm Bark_AgNP under sunlight, and D - 4000 ppm Bark_AgNP with NaBH₄ under sunlight.

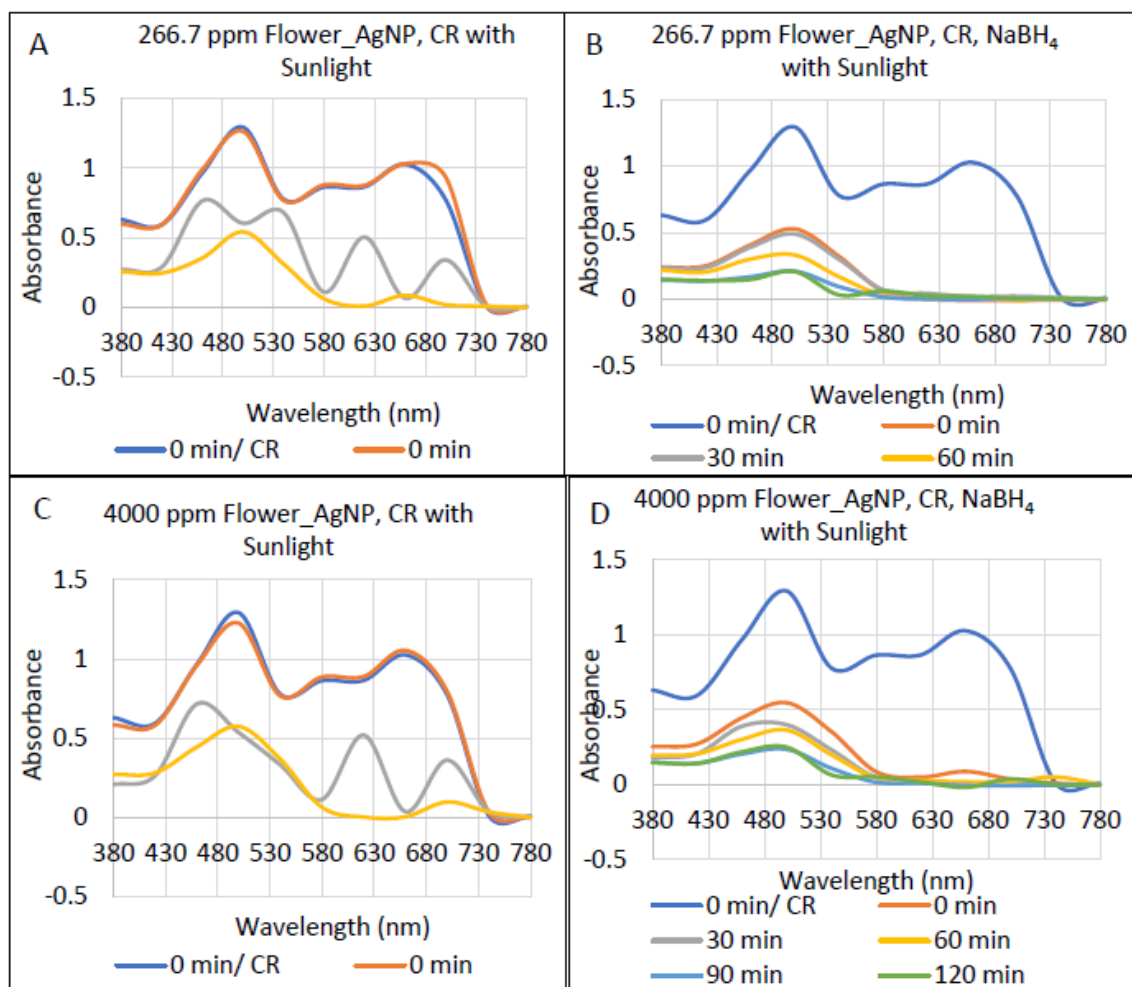


Figure 12 Photocatalytic activity of Flower_AgNP for CR; A - 266.7 ppm Flower_AgNP under sunlight, B - 266.7 ppm Flower_AgNP with NaBH₄ under sunlight, C - 4000 ppm Flower_AgNP under sunlight, and D - 4000 ppm Flower_AgNP with NaBH₄ under sunlight.

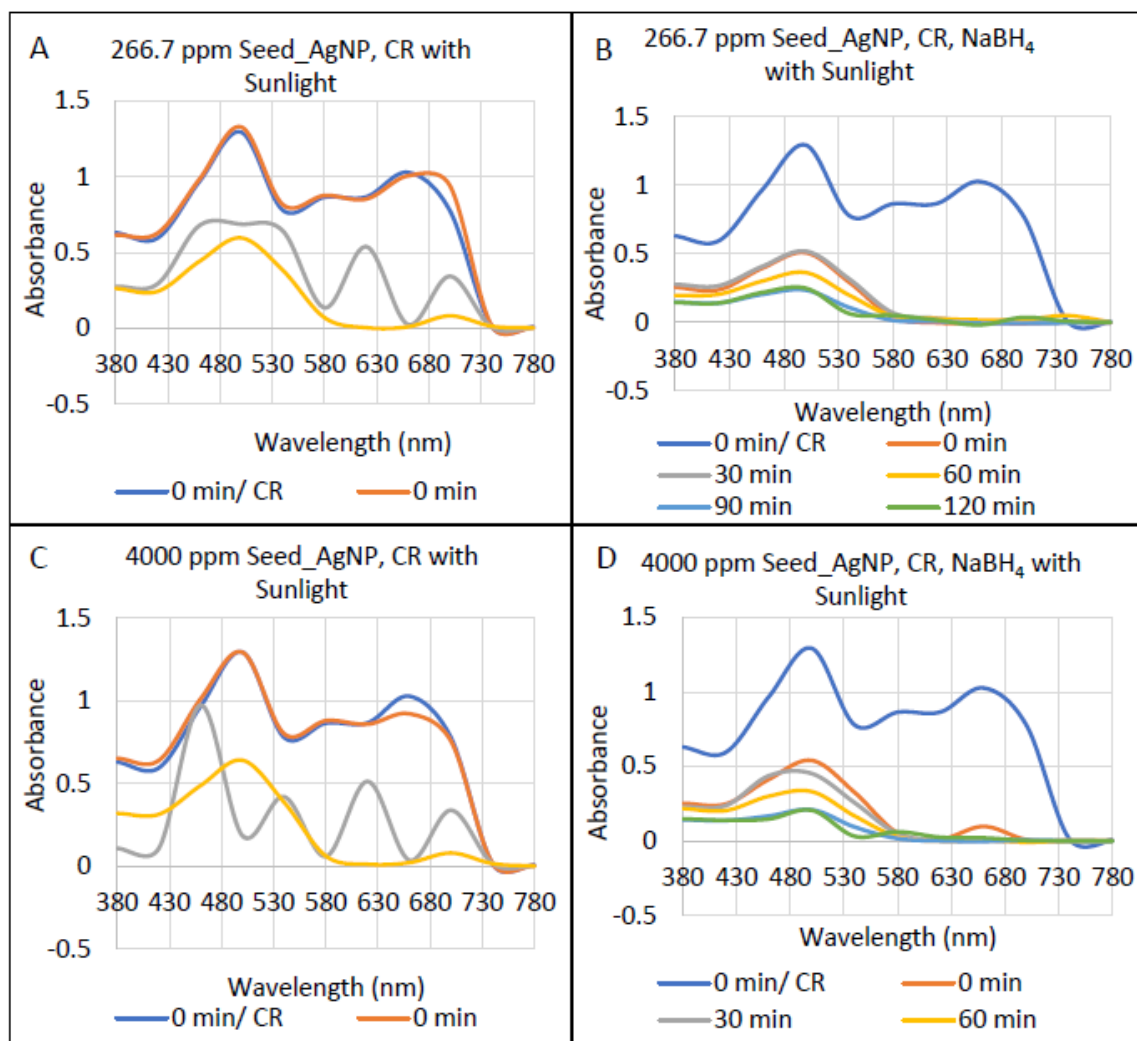


Figure 13 Photocatalytic activity of Seed_AgNP for CR; A - 266.7 ppm Seed_AgNP under sunlight, B - 266.7 ppm Seed_AgNP with NaBH₄ under sunlight, C - 4000 ppm Seed_AgNP under sunlight, and D - 4000 ppm Seed_AgNP with NaBH₄ under sunlight.

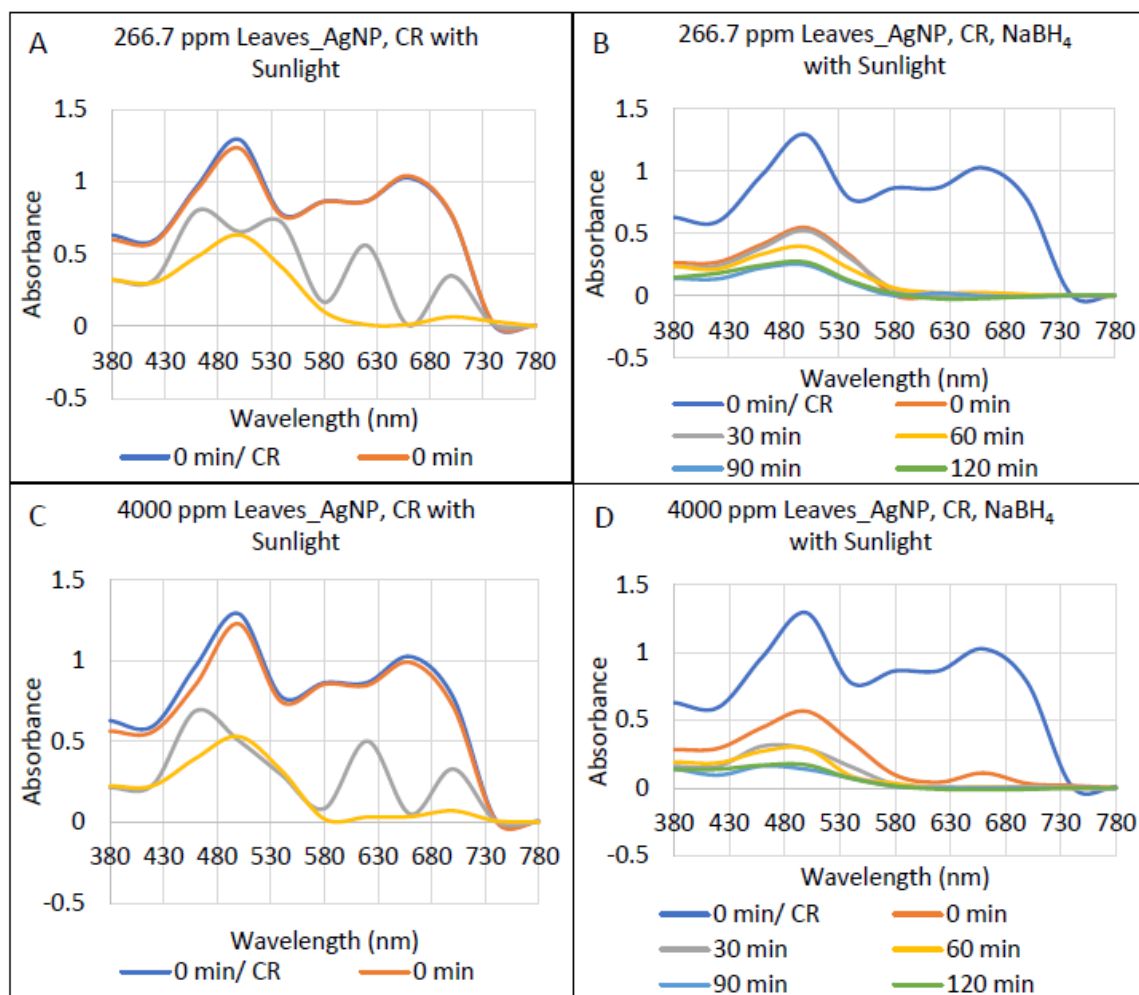


Figure 14 Photocatalytic activity of Leaves_AgNP for CR; A - 266.7 ppm Leaves_AgNP under sunlight, B - 266.7 ppm Leaves_AgNP with NaBH₄ under sunlight, C - 4000 ppm Leaves_AgNP under sunlight, and D - 4000 ppm Leaves_AgNP with NaBH₄ under sunlight.

3.4 PNP Catalysis Activity of AgNP

The PNP peak is observed at 340 nm (Figure 15). The 340 nm peak has shifted to 400 nm with the addition of NaBH₄. Only a slight degree of degradation is observed for the duration of 30 minutes (Figure 16). The addition of 20 μ L of 266.7 ppm *F. indica* AgNPs shows successful degradation of PNP except for the Seed_AgNP. The degradation is observed by the decrease in the peak at 400 nm (Figure 17).

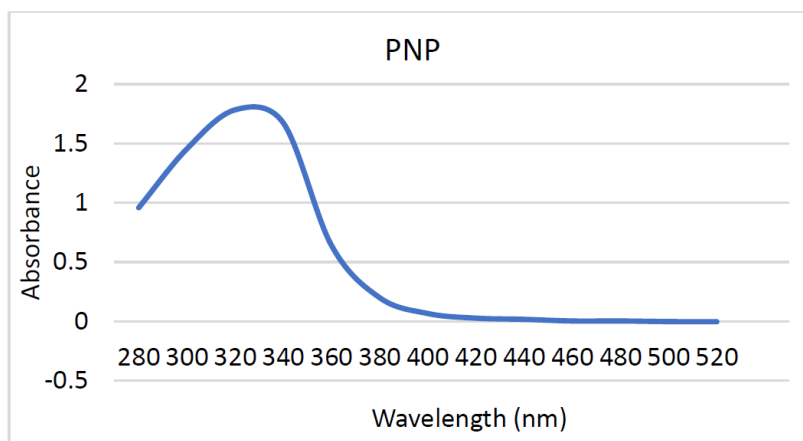


Figure 15 Absorbance spectrum of PNP.

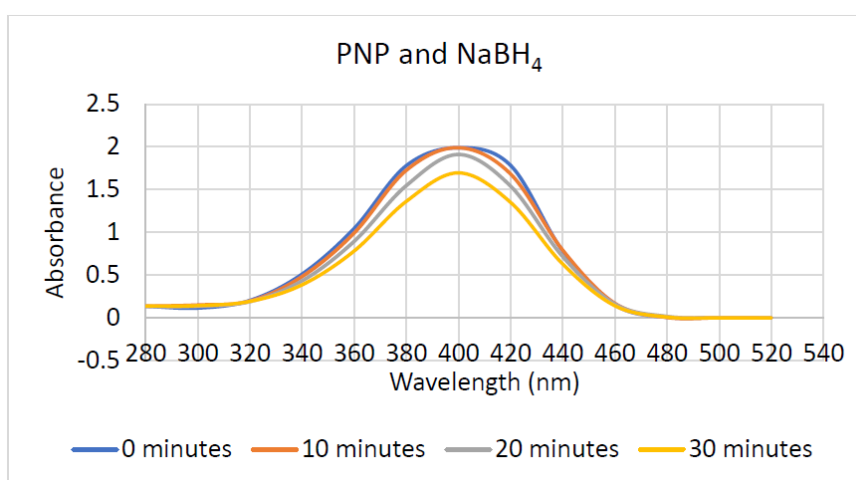


Figure 16 Absorbance spectrum of PNP with NaBH₄.

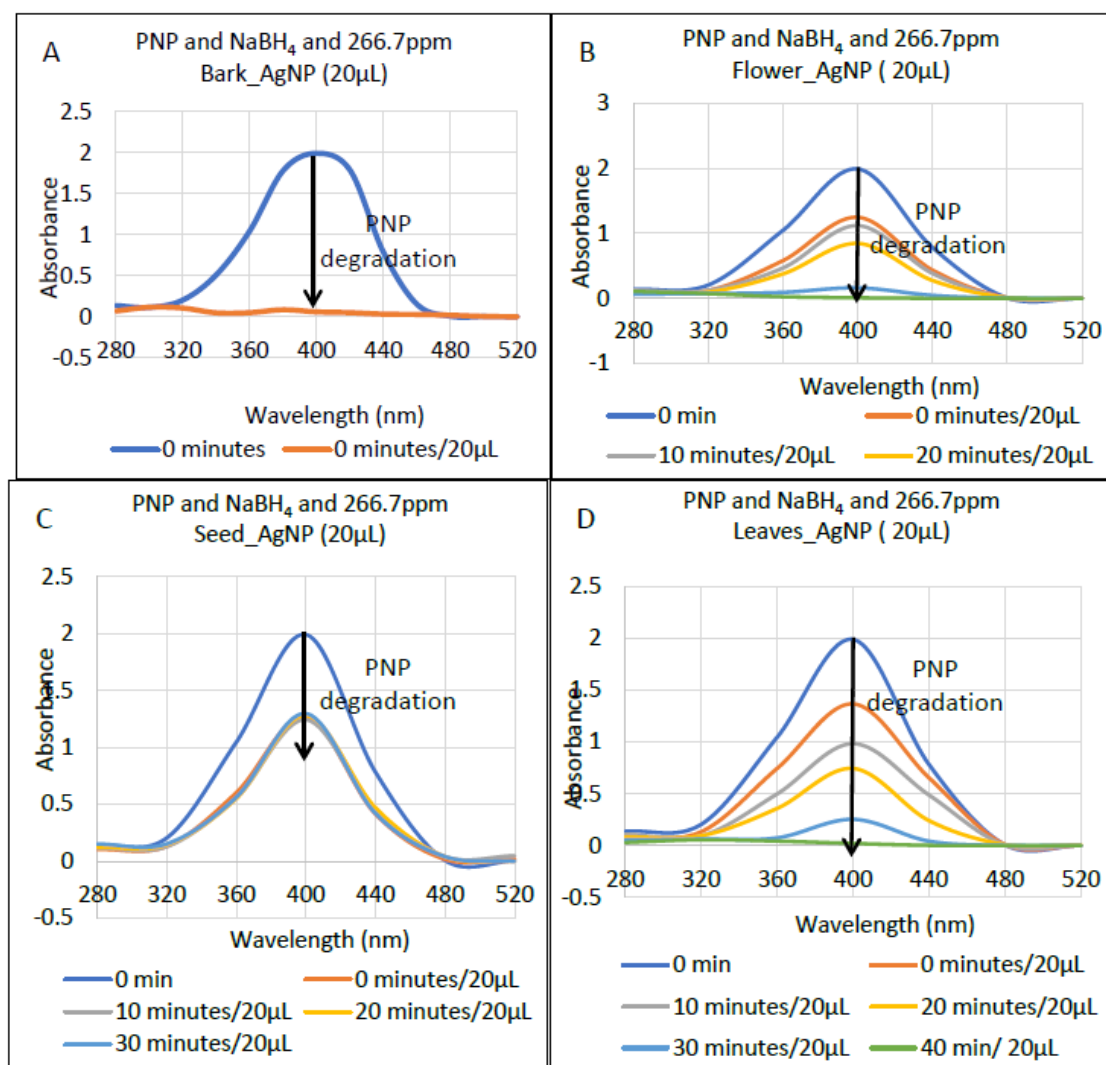


Figure 17 Catalysis of PNP by 20 µL of 266.7 ppm *F. indica* AgNPs; A - Bark_AgNP, B - Flower_AgNP, C - Seed_AgNP, and D - Leaves_AgNP.

3.5 Cytotoxicity Assay of AgNP

The shrimps showed 100% viability when incubating 800 ppm and 200 ppm concentrations of AgNP samples (Figure 18).

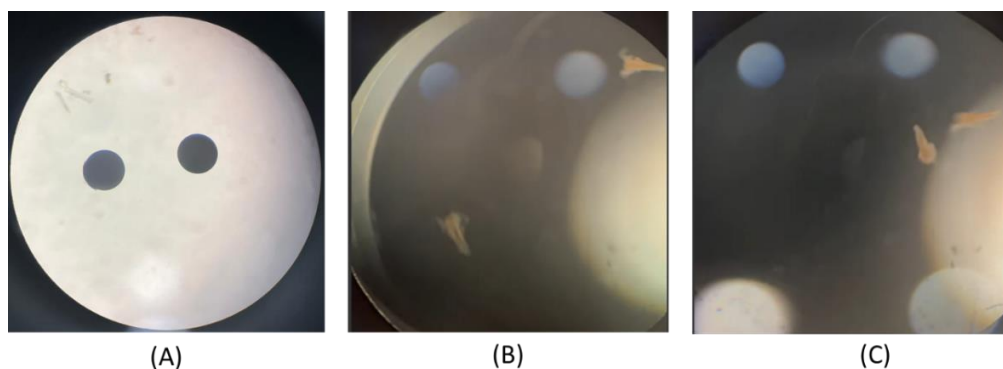


Figure 18 Microscopic image of different stages of cytotoxicity assay; A - Shrimp eggs, B - Shrimp hatchlings before incubation, and C - Shrimps after incubation (4 × 10 × 1).

4. Discussion

4.1 Green Synthesis and Formation of AgNPs

Green-synthesised AgNPs produced via low-energy, low-toxicity processes offer several advantages over conventional routes [35]. In contrast to single-part plant studies, this work systematically employs five distinct anatomical parts of *F. indica* (bark, flower, fruit, seed, and leaves) to directly assess how intrinsic phytochemical variability governs AgNP formation and functionality, demonstrating the plant's potential as a multifunctional biological precursor.

Prior to AgNP synthesis, phytochemicals or secondary metabolites in the selected plant species should be effectively extracted. This extraction can be performed using different solvents such as ethanol, methanol, DW, and dimethyl sulfoxide. DW is a highly polar solvent compared with ethanol and has proven effective for the extraction of various compounds that facilitate AgNP synthesis. In addition, water is classified under green solvents adhering to green chemistry and sustainability; it is also inexpensive, non-toxic, non-selective, and has enhanced efficiency when combined with superheating [36-38]. Using a single solvent across all plant parts ensured that observed differences in nanoparticle characteristics arose primarily from phytochemical composition rather than extraction conditions. Each extract offered distinct phytochemical profiles that influenced the size, stability, and catalytic efficiency of the resulting nanoparticles. The extracts contain secondary metabolites that play a key role in the green synthesis and stabilisation of AgNPs [39].

The secondary metabolites in the extract reduce silver ions (Ag^+) from AgNO_3 to neutral silver atoms (Ag^0) through bioreduction, facilitating the formation of AgNPs. These biomolecules act as capping and stabilising agents, preventing nanoparticle agglomeration by forming a protective organic layer on the nanoparticle surface. Extracts rich in strong reducing agents promote rapid nucleation, leading to smaller, well-dispersed nanoparticles, whereas weaker reducing environments result in slower growth and broader size distributions [39, 40].

The successful synthesis of AgNPs can be confirmed by a visible colour change, indicating the reduction of Ag^+ and nanoparticle aggregation, influencing their optical properties. This colour change originates from surface plasmon resonance (SPR), a collective oscillation of conduction band electrons induced by light excitation, and is widely accepted as a primary indicator of AgNP formation [41].

The size, yield, and morphology of AgNPs are influenced by several parameters, such as extract concentration and volume, silver nitrate concentration, temperature, and reaction time [42]. Modulating these parameters helps obtain the optimised condition necessary to synthesise *F. indica* AgNP. In this study, all parameters were held constant except temperature and time intervals; two temperatures were tested across four time intervals, along with RT. Previous research indicates that higher temperatures accelerate the reaction, promoting aggregation and the formation of smaller AgNPs, and that this is accompanied by a blue shift in the absorption spectrum, in contrast to lower temperatures. In terms of incubation time, longer incubation can cause aggregation and AgNP instability, resulting in decreased AgNP peak intensity. However, research has found that when phytochemical content is high in plant material, the incubation time required is shorter [43-45].

As per the results of this research, the optimised synthesis condition was noted as 90°C for 45 minutes (Table 1) due to the presence of a characteristic colour change (Figure 2), and an SPR peak around 460 nm for all samples except for the fruit sample (Figure 3) was confirmed by the UV-Vis

spectrophotometry. The absence of a distinct SPR band for the Fruit_AgNP sample suggests slower nucleation kinetics and incomplete bioreduction, likely due to lower concentrations of effective reducing phytochemicals or competitive complexation by sugars and organic acids. This could also be due to the agglomeration of AgNPs after the formation of stable AgNPs, which occurs beyond the optimum incubation time and weakens the SPR signal [46, 47]. These observations align with previous reports that AgNPs typically exhibit SPR absorption in the 400-450 nm range when optimally dispersed [48].

4.2 Morphology and Conductivity

SEM analysis was performed for Bark_AgNP to determine its shape and size, as these factors influence the activity of AgNPs in various applications. The results showed that Bark_AgNP was spherical, with a size range of 50nm - 70nm (Figure 4). Spherical morphology is particularly favourable for SPR-mediated catalytic processes due to isotropic electron oscillation and uniform surface energy distribution. A study by [49] on *F. jangomas*, a plant from the same genus, reported AgNP sizes ranging from 70 nm to 110 nm. The comparatively smaller size observed in this study can be attributed to stronger reducing and capping agents present in *F. indica* bark, which promote rapid nucleation and restrict particle growth.

The conductivity of AgNPs was assessed by analyzing their optical properties by measuring the band gap energy (E) from the absorbance spectrum. This represents the minimum energy required for electrons to move from the valence band (VB) to the conduction band (CB). Expressed in electron volts (eV), this parameter classifies nanoparticles by their conductivity. According to [50], nanoparticles with $E > 4$ eV are considered insulators, whereas those with $E < 3$ eV are semiconductors. All synthesized AgNPs exhibited band gap values between 2.7-3.1 eV (Table 2), confirming their semiconducting nature and suitability for photocatalytic and electron-transfer-driven reactions [51]. These values were calculated using Equation 2.

$$E = \frac{h (\text{plank's constant}) (6.626 \times 10^{-34} \text{Js}) \times c (\text{Speed of light}) (3 \times 10^8 \text{ms}^{-1})}{\lambda (\text{Wavelength of AgNP}) (10^{-9})} \quad (2)$$

Table 2 Confirming for the conductivity of optimized samples.

Sample ID	Conductivity (eV)
Bark_AgNP	2.70
Flower_AgNP	3.10
Seed_AgNP	2.95
Leaves_AgNP	3.10

4.3 Photocatalytic Degradation Mechanism of Organic Dyes

Research on nanoparticles is necessary to address the growing contamination of wastewater by dyes and other pollutants. Metal nanoparticles exhibit catalytic activity that facilitates the degradation of harmful dye molecules via electron transfer and the addition of sodium borohydride. The extent of activity depends on the metal nanoparticle's morphological characteristics. Research

has already been conducted using different plant-mediated AgNPs to evaluate their degradation capacity against common dyes such as MB, malachite green, and methyl orange [52].

The photocatalytic degradation of dyes by AgNP is mediated by electron transfer facilitated by the SPR effect. When exposed to sunlight, AgNPs absorb energy, and VB electrons get excited into the CB, creating electron-hole pairs. Dye molecules act as photosensitisers, adsorbing onto AgNP surfaces and donating electrons to the CB, enhancing the process. Excited electrons react with molecular oxygen to form superoxide radicals ($O_2^{\bullet-}$), while the holes in the VB interact with water, generating hydrogen ions and hydroxyl radicals ($\bullet OH$). These radicals break down the dye molecules into smaller, non-toxic products like carbon dioxide and water. $NaBH_4$ acts as a catalyst, which enhances the process by donating electrons to AgNPs, increasing the availability of free electrons for generating more reactive radicals and accelerating dye breakdown [53-56]. In addition, the secondary metabolites that aided AgNP stabilisation also facilitate the adsorption of dye onto the AgNP surface via hydrophobic interactions and van der Waals forces. The catalytic reduction of MB and CR, which are cationic and anionic dyes, respectively, can be monitored by changes in dye colour intensity and by decreases in the absorption peaks at 665 nm for MB and 495 nm for CR [53, 57, 58].

The photocatalytic activity of plant-mediated AgNPs can be analysed by varying parameters such as AgNP volume and concentration, dye concentration, the presence or absence of sunlight, and incubation time. Research has shown that the higher the dose of AgNP, the longer the exposure duration and direct sunlight, and the higher the degradation activity [59].

In this research, the potential of *F. indica* AgNP to perform photocatalytic degradation was studied with the use of two dyes at various conditions; two concentrations of AgNPs were used (4000 ppm and 266.7 ppm) with and without $NaBH_4$, while keeping a constant dye concentration.

The gradual decrease in the maximum absorption peaks of MB (Figure 5) and CR (Figure 10) indicated successful degradation of both dyes by *F. indica* AgNP under sunlight and in the presence of $NaBH_4$. Since the photocatalytic degradation reaction rate depends on the time, the rate of reaction/kinetics of the experiment can be evaluated under pseudo-first-order kinetics conditions (Equation 3). This model is used by previous research on photocatalytic activity between solid and liquid phases [60, 61].

$$\ln \frac{C_t}{C_0} = kt \quad (3)$$

where k is the rate constant, and C_t and C_0 represent the concentration of PNP at time interval 't' and at zero, respectively.

The MB degradation rate constants for 266.7 ppm AgNPs under sunlight alone indicate that all samples effectively degraded MB, with Flower_AgNP ($k = 0.3611 \text{ min}^{-1}$) exhibiting the highest degradation. This suggests superior photocatalytic activity at lower concentrations, which may result from smaller crystallite size and stronger SPR absorption, thereby enabling faster charge transfer. For both 4000 ppm and 266.67 ppm AgNPs under sunlight in the presence of $NaBH_4$, all samples successfully degraded MB, demonstrating the enhancing effect of the reducing agent. Bark_AgNP ($k = 0.2679 \text{ min}^{-1}$) showed the highest rate constant, implying the role of $NaBH_4$ in accelerating the degradation (Table 3, Figures 6-9). Since $NaBH_4$ is not eco-friendly, samples that degrade MB efficiently under just sunlight, like Flower_AgNP at low concentrations, are more sustainable photocatalysts.

Table 3 Rate constant values of MB photocatalysis by AgNPs.

Sample ID	4000 ppm under sunlight (min ⁻¹)	266.7 ppm under sunlight (min ⁻¹)	4000 ppm under sunlight with NaBH ₄ (min ⁻¹)	266.7 ppm under sunlight with NaBH ₄ (min ⁻¹)
Bark_AgNP	0.0456	0.0556	0.2679	0.0139
Flower_AgNP	-	0.3611	0.1627	-
Seed_AgNP	0.0613	0.1255	0.12	-
Leaves_AgNP	0.0438	0.1152	0.1823	-

In CR degradation, 4000 ppm AgNPs showed effective degradation under sunlight alone, with Seed_AgNP ($k = 0.6525 \text{ min}^{-1}$) displaying the highest rate. When combined with NaBH₄, both 4000 ppm and 266.7 ppm AgNPs efficiently degraded CR (Table 4, Figures 11-14). This suggests that AgNPs' activity depends on dye concentration and external reductants. These findings indicate that different AgNP samples show selective efficiency depending on dye type and on external factors such as NaBH₄.

Table 4 Rate constant values CR photocatalysis by AgNPs.

Sample ID	4000 ppm under sunlight (min ⁻¹)	266.7 ppm under sunlight (min ⁻¹)	4000 ppm under sunlight with NaBH ₄ (min ⁻¹)	266.7 ppm under sunlight with NaBH ₄ (min ⁻¹)
Bark_AgNP	0.1852	-	0.1174	0.2007
Flower_AgNP	0.1833	-	0.1139	0.1374
Seed_AgNP	0.6525	0.1742	0.1172	0.1764
Leaves_AgNP	0.2654	-	0.1959	0.1556

The overall efficiency of the photocatalytic degradation reaction depends on factors such as particle size, crystallinity, and surface capping, which influence how quickly electron-hole pairs recombine. The strong photocatalytic performance observed for *F. indica*-AgNPs therefore likely results from their optimised nanostructure and the stabilising effect of phytochemical residues, which facilitate charge transfer and improve catalytic stability during light exposure [62, 63]. The SPR characteristics of AgNPs are highly dependent on particle size, morphology, aggregation state, and surface modification by phytochemical capping agents [64, 65]. These surface-bound biomolecules contribute to nanoparticle stabilization by limiting agglomeration and simultaneously influence surface electron distribution, thereby facilitating improved charge transfer during catalytic and photocatalytic reactions [66, 67]. Accordingly, the observed differences in SPR intensity and catalytic efficiency among AgNPs synthesized from different plant parts can be attributed to variations in nanoparticle morphology and surface chemistry arising from distinct phytochemical compositions [68].

Photocatalysis using *F. indica* AgNPs has not been widely explored for any azo dyes. In a related study, [69] reported that *F. indica*-based P-ZrO₂CeO₂ZnO nanoparticles degraded CR under UV light. There is no documented research on *F. indica* AgNPs or any other plant in the same family, and their potential in dye degradation. However, various studies have shown that plant-synthesized AgNPs exhibit high degradation rates, both with and without NaBH₄, following first-order kinetics. These

results were obtained for other common dyes such as methyl orange, methyl red, carmoisine, tartrazine, and rhodamine B [70, 71].

In contrast, the present study demonstrates that AgNPs synthesized from *F. indica* effectively degrade CR under natural sunlight, highlighting the advantage of SPR-driven photocatalysis. Since this process operates efficiently under visible light, it offers a sustainable, energy-efficient alternative for the degradation of organic dyes without requiring artificial UV irradiation. However, further experiments can evaluate the degradation potential under artificial UV irradiation and vary other experimental parameters to elucidate the optimized conditions required for the synthesized *F. indica* AgNPs to function.

4.4 Catalytic Reduction of PNP

AgNPs catalyse the degradation of PNP in the presence of NaBH_4 by lowering the activation energy and transferring six electrons per PNP molecule. This process is surface-mediated and depends strongly on nanoparticle accessibility and electron-relay efficiency. Although the conversion of PNP to para-aminophenol (PAP) is energetically favourable, it remains kinetically slow when only NaBH_4 is present, due to an energy barrier between the borohydride ion (BH_4^-) and the p-nitrophenolate ion ($\text{NO}_2\text{-PhO}^-$) [72, 73]. Differences in catalytic performance among AgNP samples reflect variations in surface chemistry, particle size, and availability of active sites. During the PNP degradation process, the initial PNP peak at approximately 320 nm shifts to 400 nm upon the addition of NaBH_4 . This is due to the formation of the p-nitrophenolate ion, as confirmed by the decolourisation of the PNP solution. In the absence of AgNP, this reaction is slow. AgNPs overcome this limitation by facilitating electron transfer between the two ions and providing a surface for ion adsorption, while also allowing PAP to desorb once produced. Additionally, the repulsion between p-nitrophenolate ions and borohydride ions is diminished due to the fast electron transfer by AgNPs. The formation of PAP is observed by the formation of a new peak between 281 and 314 nm [3, 74].

These results show that the addition of AgNPs, except for Seed_AgNP, led to complete degradation of PNP within 40 minutes (Figure 17). Since the concentration of NaBH_4 was higher than the concentration of PNP, the experiment's kinetics were analysed using first-order kinetics (equation 3). It can also be assumed that the NaBH_4 concentration is constant throughout the experiment [75].

The observed order of catalytic efficiency, Bark > Flower > Leaves, indicates that phytochemical richness and nanoparticle size collectively control the kinetics of reduction (Table 5). The high surface area and active sites of smaller Bark_AgNP promote rapid adsorption and charge transfer, explaining their immediate degradation activity. This suggests that *F. indica* AgNPs are an efficient catalyst and may prove useful in environmental remediation.

Table 5 Rate constant values of PNP catalysis by AgNPs.

Sample ID	Rate constant (min^{-1})
Bark_AgNP	Immediately degraded
Flower_AgNP	0.5031
Leaves_AgNP	0.4216

4.5 Cytotoxicity and Biocompatibility

The biocompatibility of synthesized AgNPs depends on their cytotoxicity and is critical for sustainable environmental use. Uncontrolled release of silver ions is a major contributor to AgNP-induced toxicity in aquatic organisms. AgNPs release Ag^+ ions, which can induce toxicity in *A. salina* when ingested. Interactions between AgNPs and the protective chitin-rich outer cuticle layer alter their structure, potentially causing toxicity and mortality [24, 28, 76]. The leaching of Ag^+ ions is the sole cause of toxicity. Studies have also focused on the control of Ag^+ ion release to upgrade the long-term performance, biocompatibility, and environmental friendliness of synthesized AgNPs. These conventional control mechanisms include the incorporation of AgNPs with mesoporous matrices, polymeric membranes, hydrogels, encapsulation systems, and fibres. These methods act as a barrier to prevent Ag^+ ion leaching and reduce toxicity [64, 77-79]. However, in this research, *F. indica* AgNPs were tested for toxicity with the use of phytochemicals capped around them and without the use of these synthetic additions. These phytochemical capping layers likely restricted Ag^+ ion leaching, reducing oxidative stress and enhancing environmental compatibility [80].

To assess cytotoxicity, a brine shrimp lethality test was conducted. Viability, calculated using Equation 1, is the percentage of organisms that survived 24 hours of exposure. In this study, different concentrations of the synthesised AgNPs, 800 ppm and 200 ppm, were utilised to gain a basic understanding of how concentration-dependent cytotoxicity is observed. The experiment showed 100% viability at both concentrations (Figure 18), confirming the non-toxicity of the AgNPs.

Cytotoxicity studies have not been conducted using the brine shrimp assay for *F. indica* plant species; however, cytotoxicity was evaluated using cancer cell lines, particularly Dalton's Lymphoma Ascites cells, with significant anti-proliferative activity (70-75% cell death at 50-100 $\mu\text{g/mL}$) and *Populi gemmae* AgNPs which belongs to the same family reported antiproliferative potential against lung adenocarcinoma cell line and human breast adenocarcinoma [14, 81]. This highlights that AgNPs' cytotoxicity is cell-type dependent, as they remained non-toxic to *A. salina*, indicating their biocompatibility in non-cancerous models. Further studies should be performed on different model organisms to properly understand the extent of cytotoxicity of these *F. indica* AgNPs, as the viability can change depending on the experimental organisms and also the concentration of AgNPs to which they are exposed.

5. Conclusions

This study demonstrates the successful green synthesis of AgNPs using different parts of *F. indica* – bark, flower, fruit, seed, and leaves – an eco-friendly process driven by the plant's phytochemical composition acting as natural reducing and stabilising agents. Among the selected plant parts, bark, flower, seed, and leaves successfully synthesised AgNPs at 90°C for 45 minutes, confirmed by a standard colour change and a characteristic peak at 460 nm. Morphological analysis using SEM revealed spherical Bark_AgNP between 50 nm and 70 nm, while conductivity analysis confirmed semiconducting behaviour. The photocatalytic efficiency of these *F. indica* AgNPs was observed with MB and CR dyes. The highest degradation with MB was observed for Flower_AgNP at 266.67 ppm under sunlight ($K = 0.3611 \text{ min}^{-1}$) and for Bark_AgNP at 4000 ppm under sunlight ($K = 0.2679 \text{ min}^{-1}$). With regard to CR, an exceptionally high degradation rate was observed with 4000 ppm Seed_AgNP under sunlight. These results highlight the effectiveness of the SPR effect, the difference in dye molecules, and other experimental parameters in the degradation process. Bark_AgNP degraded

PNP immediately, followed by a high rate of degradation in the flower and the seed. The cytotoxicity evaluation using *A. salina* confirmed that 800 ppm and 200 ppm of synthesised *F. indica* AgNPs were non-toxic, indicating their biocompatibility and environmental safety. Overall, the findings establish *F. indica* as a promising biological resource for sustainable nanocatalyst development, offering a green, low-cost, and efficient approach for environmental remediation applications.

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Author Contributions

Dean and senior supervisor Dr. Mathivathani Kandiah carried out the planning and design of the research and analyzed with revision of manuscript. Experiments were executed and recorded by Nasmah Nisthar. Beneli Gunaratne and Ominda Perera have overlooked the experiment work.

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Competing Interests

The authors have declared that no competing interests exist.

Data Availability Statement

Data relevant to this research can be requested from the authors at mathi@bms.ac.lk.

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