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A detailed investigation of the catalytic abilities and adsorption curves of Banana peel with nanodendrite Silver nanoparticles for wastewater purification

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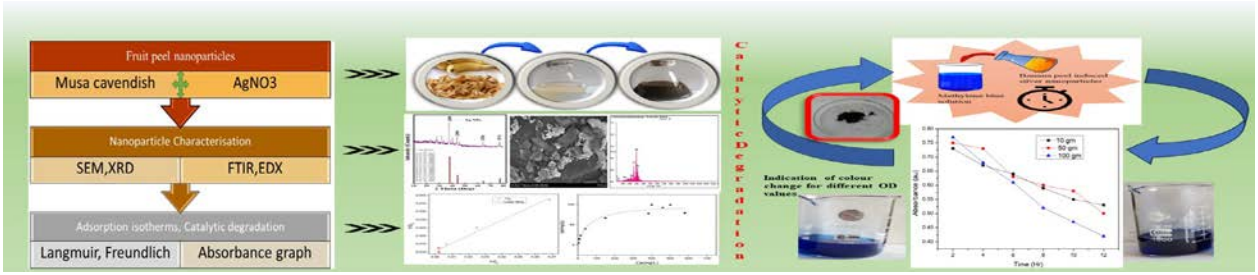
Article

ABSTRACT



In this investigation, banana peel extract (Musa cavendish) (BPE) was used to produce silver nanoparticles. The paper presents a green method for the synthesis of silver nanoparticles from bananas. In this all-natural synthesis, biodegradable silver nanoparticles were produced using BPE as a reducing agent. The addition of the aqueous banana peel extract to the silver nitrate solution caused a change in the colour of the reaction medium from pale yellow to brown, indicating the reduction of silver ions to silver nanoparticles. Further analysis of the AgNPs was carried out using XRD, FTIR and SEM techniques. XRD was used to determine the crystalline nature and purity of the silver nanoparticles produced. The Langmuir adsorption isotherm showed that the adsorption takes place in a monolayer. It was found that the silver nanoparticles synthesised using green methods were effective in degrading the pollutant at different exposure times. Nanoparticles have enhanced surface properties and chemical activity, making them effective in removing or degrading dye material from wastewater during treatment.

Keywords: Banana peel, Nanodendrites, Isotherms, Methylene degradation

INTRODUCTION

Access to clean water is a fundamental human need. The scarcity of safe water resources is caused by the rapid growth of the global population, climate change, and the accelerated depletion of natural water supplies. To address this issue, it is essential to use water resources efficiently, treat wastewater for industrial and agricultural use, and promote affordable and environmentally friendly solutions. The technologies mentioned are effective in maintaining the world's clean water supply and promoting sustainable conservation of limited freshwater resources.[1,2] Heavy metals in water sources present a global challenge due to their toxicity to living organisms, lack of biodegradability, and tendency to accumulate in biota. They can also impair the immune system, cause cancer, and pose a threat to life on earth.[3] In light of the significant threat posed by heavy metal ions to the environment and to human health, researchers are compelled to seek new strategies for their remediation. Among the metal nanoparticles, silver nanoparticles (AgNPs) have gained significant interest due to their excellent catalytic activity, chemical stability, high thermal properties, and nonlinear optical behaviour.[4,5] Biosynthesis represents an enhanced method for reducing silver to nanoparticles, utilising agricultural waste.[6] A range of adsorbents, including clays, agricultural waste, carbon nanotubes, silica, polymers, and activated carbon, have been investigated for the removal of heavy metal ions from wastewater.[6,7] Adsorbents derived from agricultural waste are widely available, environmentally friendly, and effective over a wide pH range, rendering them suitable for a

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variety of environmental conditions. Nevertheless, their relatively slow adsorption and weak affinity for heavy metals have prompted researchers to investigate chemical modifications of these adsorbents.[8] Several studies have demonstrated the effectiveness of using silver nanoparticle composites as adsorbents to remove organic and heavy metal ions from aqueous solutions.[9] However, their limited stability and tendency to agglomerate may restrict their applicability in wastewater treatment.[10,11] AgNPs are held by mechanical support, such as banana leaf powder (BPW), for potential wastewater treatment applications. BPW is an abundant and ecological agricultural waste that can be used as an adsorbent.[12] Silver ions were infused into BPE using its inherent porosity, followed by the reduction of silver ions to silver nanoparticles. To enhance adsorption efficiency, we utilized both banana peel extract (BPE) and silver nanoparticles (AgNP) to prevent AgNP aggregation and release into solution. BPE, with its high oxygen density serving as a binding site for AgNPs, was employed to trap AgNPs. The bioactive compounds found in banana peel, such as chlorophyll-A, phenolic acids, flavonoids, and β carotene, were identified.[13] The objective of this work is to create a composite of BPW and AgNPs that combines the advantages of both BPE and AgNPs for the removal of methylene blue from aqueous solutions. The study investigates the effect of initial metal ion concentration, adsorbent dose, and adsorption isotherm on methylene blue uptake.

Materials

Banana peels were collected from a local supermarket in Koyambedu, Chennai, India. For dye degradation experiments, silver nitrate (99.8%, Kishida) and Methylene blue were used. Experimental solutions were prepared using double distilled water.

Preparation of Banana peels extract

Fruit peels were collected from a local supermarket and processed for further use. The peels were cut into small pieces and washed with tap water for 5-10 minutes, followed by a wash with distilled water for 20 minutes to remove impurities. After drying at 100°C for 24 hours, the peels were ground into a fine powder and sieved through a 1.40 mm sieve. To prepare the extract from banana peel, 10 g of banana peel powder was mixed with 200 mL of distilled water. The mixture was then shaken for 1 hour and left to incubate overnight. The resulting solution was filtered through a Whatman No. 4 filter and stored in a conical flask for use in nanoparticle synthesis.

Synthesis of silver nanoparticles (AgNPs) using banana peel extract

At room temperature, 20 mL of banana peel was mixed with 80 mL of 1 mM AgNO3 aqueous solution (0.013 g). The solution was stirred on a magnetic stirrer for 1 hour. After incubating the final solution (AgNO3 - BPE) in the dark for 24 hours, a brown color change indicated the formation of nanoparticles14. Additionally, the formation of silver nanoparticles was confirmed by a strong SPR band at 400-450 nm in the UV-Vis spectrum.

Preparation of Methylene blue solution

To prepare a 2.5 ppm solution of methylene blue, the appropriate amount of methylene blue solution was mixed with distilled water. For a 500 ml solution, 0.312 g of methylene blue solution was used. The dye solution was then placed in a shaker for one hour to ensure uniform dispersion. After one hour, the solution was divided into five 100 mL flasks. In each flask, various concentrations (0.02 mL, 0.04 mL, 0.08 mL, 0.16 mL, 0.32 mL) of AgNPs-BPE nanoparticles were synthesized and mixed. The flasks were placed in a shaker for one hour. A comparative study was conducted by repeating the same procedure with varying weights of banana peel mixed with methylene blue solution.

Figure 1. Colour change from pale yellow to brown indicates the synthesis of silver nanoparticles

Characterization Techniques

The spectra of the solution were obtained using a UV-5800PC spectrophotometer and quartz cuvettes in the wavelength range λ = 190-700 nm. Particle size was determined using scanning electron microscopy, while XRD (Rigaku SmartLab X-ray diffractometer) was used to determine crystallinity. Surface morphology studies were conducted using SEM(JEOL JSM-6510LV) analysis. Additionally, FTIR (Thermo Scientific (Bruker Vertex 80) FT-IR spectrophotometer) spectra were generated for both banana peel and synthetic nanoparticles. The study analysed the presence of silver nanoparticles synthesized through energy dispersive X-ray analysis.

Results and discussion

Analysis of SEM

SEM was used to examine the surface morphology of synthetic banana peel with silver nanoparticles. The particles are aggregated in a nano dendritic manner, as shown in Figure 1. The produced nanoparticles have an average size of 29.7 nm. [15]Conducted a study exclusively on nano dendrite-shaped gold particles for various applications. They presented SEM micrographs illustrate the formation of dendritic structures with varying dimensions. Additionally, randomly distributed single Ag rounded nanoparticles with an average diameter of 33 ± 6 nm were observed, which is higher than that of the commercial standard AgNPs. In their 2011 study, [16]investigated the successful synthesis of various single-crystalline Ag nanostructures, such as dendrites, dendritic flowers, and cactus-like rods, through a simple, facile, and cost-effective method based on the galvanic replacement reaction.

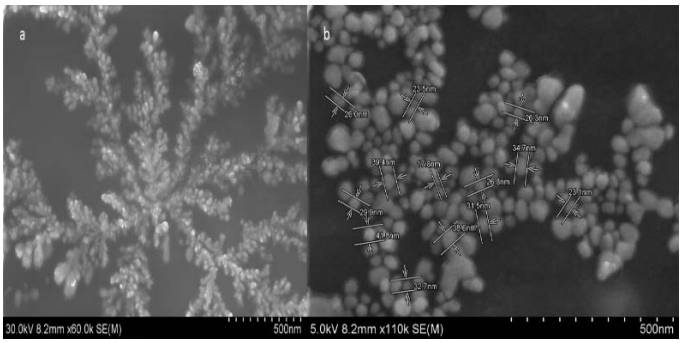


Figure.2. SEM images of nano dendrites

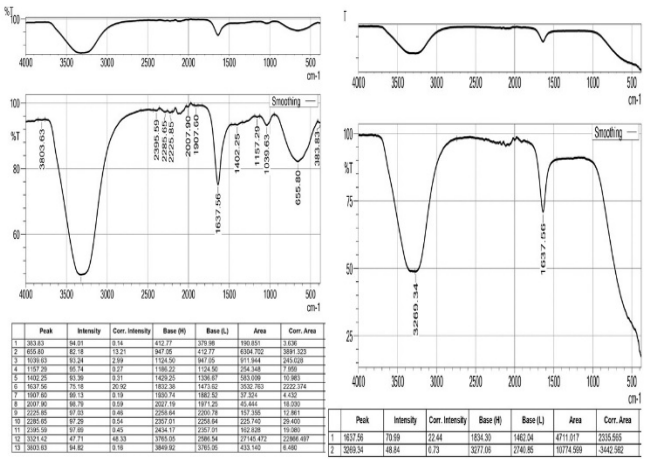
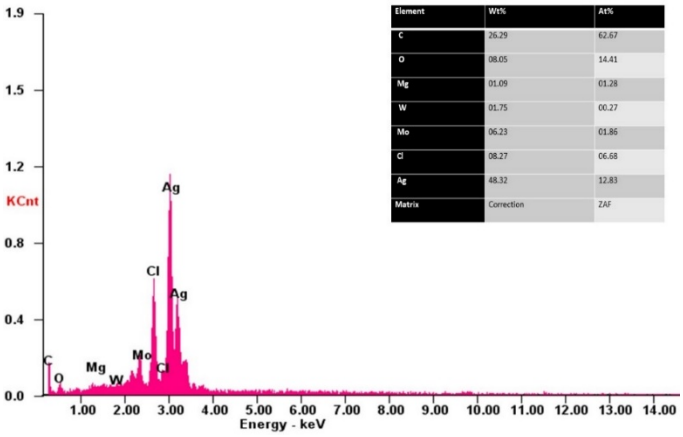


Figure 3. FTIR spectra before synthesis and after synthesis of $AgNO_3$-BPE



Element	Wt%	At%
C	26.29	62.67
O	08.05	14.41
Mg	01.09	01.28
W	01.75	00.27
Mo	06.23	01.86
Cl	08.27	06.68
Ag	48.32	12.83
Matrix	Correction	ZAF

Figure 4. EDX analysis of synthesized nanoparticle

FT-IR ANALYSIS

FT-IR analysis was conducted to identify the main functional groups present in the surface structure of BPE and their possible involvement in the synthesis and stabilization of silver nanoparticles. The spectra of BPE before and after the reaction with silver nitrate are shown in Figure 3. The control spectrum (BPE untreated with AgNO3) exhibited multiple peaks, indicating the complex nature of the biological material. Bands were observed at

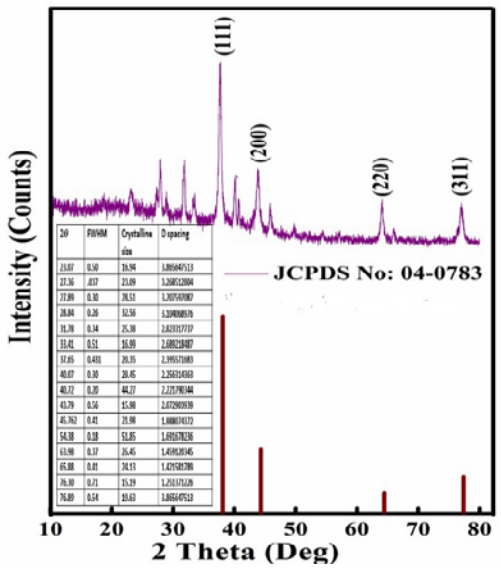


Figure 5.XRD data of synthesized AgNO3-BPE nanoparticle

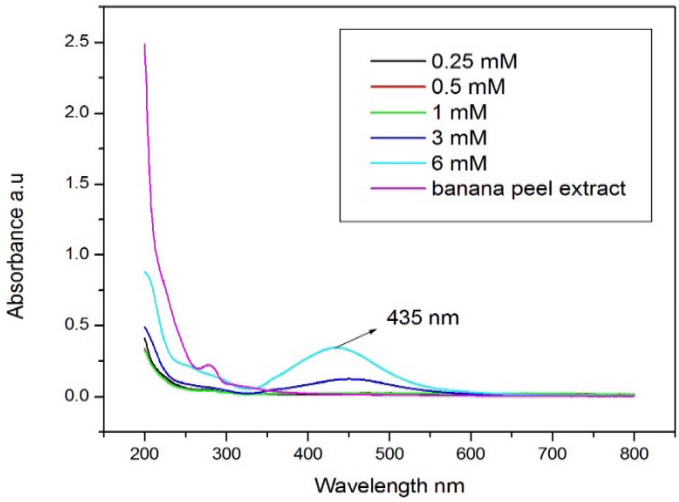


Figure 6. UV-Vis spectra at different concentrations of AgNPs

3411, 2932, 2395.5, 2285.65, 2225.85, 2007.9, 1907.6, 1637.56, and 655. The infrared spectrum showed peaks at 80 cm-1 which were assigned to various functional groups including O-H stretching vibrations of alcohols and carboxylic acids, C-carboxylic acid or alcohol ester, N-C==O amide I bond of proteins, CH_2 alkanes, C-O carboxylic acid, ester or ether, C-N of aliphatic amines or alcohol/phenol, N-H distortion of amines, and C-C bending. Following the reaction with $AgNO_3$, there was a shift in the peaks as follows: The spectral analysis showed absorption bands ranging from 3411 to 3269.34 cm^{-1}, indicating the involvement of carboxyl, hydroxyl, and amide groups present on the surface of BPE in the process of nanoparticle synthesis[17]. Banana peels are primarily composed of pectin, cellulose, and hemicellulose.[18] The functional groups associated with these polymers, as well as protein matter, can participate in the reduction of Ag^+ to Ag^0. Metal salts are known to interact with biological

components through functional groups, which mediate the reduction of metal salts to nanoparticles.[19]

EDX analysis

The EDX analysis provides both qualitative and quantitative information on the elements involved in the formation of nanoparticles. The elemental profile of the synthesized nanoparticles using BPE indicates a higher count of silver at 3 keV, which confirms the formation of silver nanoparticles. Typically, metallic silver nanocrystals exhibit an optical absorption peak at around 3 keV due to their surface plasmon resonance.[19] The elemental analysis of the silver nanoparticles, as shown in Figure 4, revealed that silver had the highest proportion, followed by chlorine and magnesium.

XRD analysis

X-ray diffraction spectra were used to obtain the AgNPs-BPE lattice structure, as described in Figure 5. The lattice's (111) plane is strongest at 37.65°, with (200) peaking at 45.75°, (220) at 65.88°, and (311) at 76.89°. This confirms that the AgNPs have a face-centered cubic lattice structure. The crystalline structure of AgNP was confirmed using X-ray diffraction analysis.[20] The X-ray diffractogram shows that metallic silver has a face-centered cubic (fcc) structure with four distinct and well-defined intense diffraction peaks corresponding to the (111), (200), (220), and (311) lattice planes. These peaks are observed at scattering angles (2) of 37.5°, 44.6°, 64.44°, and 76.45°, respectively.[21] No other prominent peaks in the XRD patterns were observed, indicating that silver is the primary constituent of the nanoparticles.[22] Also demonstrated the synthesis of silver nanoparticles at 25°C, with three intense peaks corresponding to (111), (200), and (220) planes. These intensities were in good agreement with the unit cell of the face-centered cubic (FCC) structure of metallic silver (Joint Committee for Powder Diffraction Standards, JCPDS File No. 04-0783). Furthermore, the results demonstrate that the production of silver nanoparticles at a temperature of 60°C yields three distinct peaks at 38.42, 44.22, and 64.68, corresponding to the (111), (200), and (220) planes. The average crystalline value, calculated using the Scherrer formula $D=(k\lambda/\beta \cos\theta)$, is 25.821.

UV- Visible spectroscopy analysis

The analysis of the UV-Vis spectrum and the significance of AgNO3 indicate that the banana peel contains the necessary elements to generate silver nanoparticles (Fig 6). The concentration of banana peel extract increases proportionally with its absorption capacity. Additionally, it was observed that the surface plasmon peak at 428 nm gradually shifts towards 435 nm at higher concentrations. This shift may be due to a blue shift, which depends on the size and shape of the particle.[23,24] Attribute the presence of a band to the absorption of colloidal silver nanoparticles in the 400-450 nm range due to surface plasmon vibrations. The number of compounds required to reduce Ag^+ to Ag^0 increases with a high concentration of banana peel extract.

ADSORPTION ISOTHERMS

Langmuir isotherm

Langmuir put up a theory to explain the sorption of gas molecules onto metal surfaces. The Langmuir isotherm in linear form is given by:

$$\frac{1}{\mathrm{Qe}} = \frac{1}{\mathrm{Qm}b * Ce} + \frac{1}{Qm}$$

where Qm is the monolayer sorption capacity of the sorbent (mg/g), Qe is the equilibrium dye concentration on the sorbent (mg/g), Ce is the equilibrium concentration of dye in the solution (mg/L), and b is the Langmuir sorption constant (l/mg) related to the free energy of sorption. The Langmuir adsorption isotherm suggests monolayer coverage of adsorbed molecules.[25] (Figure 6) displays the Langmuir plots of the methylene blue sorption isotherm for various initial dye concentrations. In Table 1, the constants Q_m and b are listed. The affinity between sorbent and sorbate is indicated by the constant b. The qualities of an excellent sorbent include a high Qmax and a high R^2 (0.9198) . The results showed that both homogeneous and heterogeneous sites are required to carry out the process of adsorption, which is consistent with the aforementioned isotherm model.[26] The Langmuir isotherm suggests that there was likely chemical adsorption by the ion exchange mechanism, which is suggestive of the homogenous monolayer distribution of the active sites.

Table 1. Isotherm constants for the decolorization of Methylene blue by AgNPs

Isotherm model	Parameters	Values
Langmuir	q_{max}	65.5261 mg/g
	B	0.1023
	R^2	0.9198
Freundlich	K_f	12.79
	1/n	0.389
	R^2	0.8126
Temkin	K_t	12.10
	B	1.75
	R^2	0.867

Freundlich isotherm

The heterogeneous systems are represented by an empirical equation of the Freundlich isotherm, and the linear form of the Freundlich isotherm is represented by the equation:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$

where K_f is a constant relating to the sorption capacity and 1/n is an empirical parameter relating to the sorption intensity, which varies with the heterogeneity of the material. K_f value of 12.79 and 1/n value of 0.389 were obtained from the plot. A value of 1/n between 0 and 1 indicates good sorption.[27] The current investigation found a value of 0.3957, demonstrating successful sorption of Methylene blue dye onto the AgNPs. The Methylene Blue Sorption Isotherms are displayed in Figure 7 at various Freundlich initial dye concentrations, and the constants Kf and 1/n are listed in Table 1. The slope value on the plot of log Qe vs log Ce corresponds to K_f, and the intercept value corresponds to 1/n. The Freundlich isotherm generally does not account for saturation of the adsorbent by the sorbate and predicts infinite surface coverage, indicating multilayer sorption on the surface. The Freundlich constant (1/n) of 0.3957 estimates the adsorbent's surface heterogeneity, which is reflected in physical sorption.

However, the R^2 of the Freundlich isotherm is smaller compared to the Langmuir isotherm model. Therefore, the Langmuir isotherm better fits the experimental data than the Freundlich isotherm.

Temkin isotherm

The representation of Temkin isotherm is as follows:

$$Q_e=\frac{RT}{b}\ln KT+\frac{RT}{b}\ln C_e$$

or

$$Q_e=B\ln KT+B\ln C_e$$

where constant B = RT/b, which is related to the heat of sorption, R is the universal gas constant (kJ/mol K), T is the temperature (K), b is the variation of sorption energy (J/mol), and K T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. Table 1 presents the values of the constants B and K T obtained from the plot of Q_e versus ln C_e in Figure. 4. The Temkin isotherm model considers the interactions between the adsorbent and adsorbate during adsorption.[28] This model assumes a uniform distribution of adsorbate and linearly decreasing heat of adsorption of all molecules in the layer with molecule coverage due to adsorbate-adsorbate repulsions. The constant B, associated with the heat of adsorption and KT, represents the maximum binding energy. The correlation coefficients indicate that the Temkin model was a better approximation to the experimental results than the Langmuir model. Therefore, out of the three isotherm models used, the Langmuir model provides the best correlation factors.

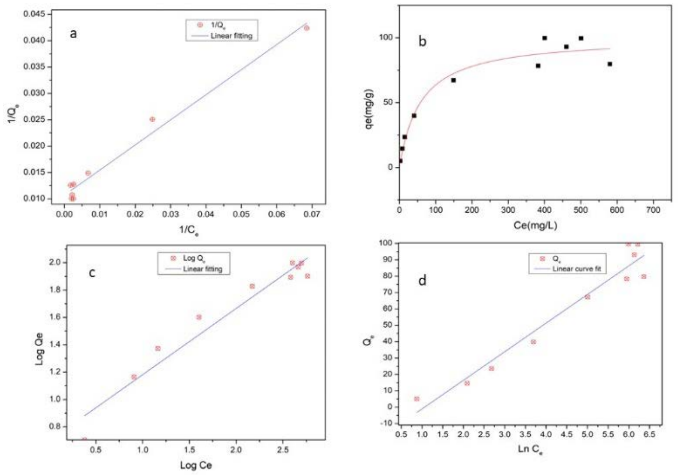


Figure 7. (a-b) Langmuir isotherm plot for the sorption of Methylene blue onto AgNPs, c) Freundlich isotherm for the sorption of Methylene blue onto AgNPs,d) Temkin isotherm plot for the sorption of Methylene blue onto AgNPs

CATALYTIC DYE DEGRADATION USING SILVER NANOPARTICLES

The capability of green-generated silver nanoparticles to degrade catalytically was investigated by creating a certain concentration of methylene blue solution. Green synthetic nanoparticles were added to the generated solution, and the degradation was observed at various concentrations. Colorimetry can be used to monitor methylene blue transformation into an inert state. OD values were measured for 24 hours at various concentrations. According to this procedure, including nanoparticles enhances the degrading property. The graphs below display the banana peel silver nanoparticles' degradation potential.

Table 2. OD values of different concentrations for different time intervals

Concentration (mg)/OD		9.00 AM	11.00 AM	1.00 PM	3.00 PM	5.00 PM	7.00 PM	9.00 PM
Day 1	10	0.73	0.67	0.64	0.59	0.55	0.53	.5
	50	0.75	0.73	0.63	0.60	0.58	0.50	.47
	100	0.77	0.68	0.61	0.52	0.47	0.42	.37

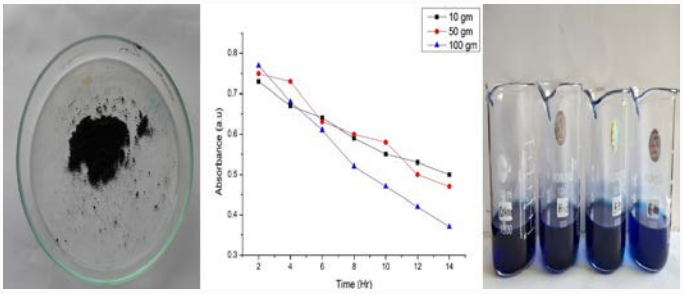


Figure 8. Absorbance graph and visual observation of degradation of Methylene blue

CONCLUSION

Nature has efficient ways of producing valuable resources. The development of environmentally friendly procedures has been driven by the increasing awareness of green chemistry and the use of green routes for synthesizing metal nanoparticles, particularly silver nanoparticles.[29] The use of banana peel extract as a catalyst for green synthesis is both simple and environmentally beneficial. The experiment revealed that color change from dark blue to a less bluish shade and degraded as the dosage increased. The addition of varying amounts of silver nanoparticles to the methylene blue solution resulted in significant color changes. The rate of degradation increased with the concentration of nanoparticles, with maximum degradation observed when 100 mL of silver nanoparticles were added to the methylene blue solution. Visual observation of the methylene blue solution revealed an atypical colour change even with increasing concentration of nanoparticles. A comparison between banana peel extract and plot analysis indicates that non-linear absorption increases in direct proportion to total concentration. There is significant interest in advancing green synthesis due to its cost-effectiveness, environmental friendliness, and ease of large-scale synthesis compared to chemical and physical methods. A centrifuge was utilised to separate the nanoparticles. The identification of the nanoparticles was carried out using UV-vis, XRD, FT-IR, SEM, and EDX spectra. The exposure of the solution to banana peel extract resulted in the reduction of Ag^+ to Ag^0, which caused the solution to change colour from colourless to dark brown. The AgNPs-BPE nano

synthesis and catalytic degradation experiments were highly effective in removing approximately 85% of the dye, making it an efficient water filtration method.

CONFLICT OF INTEREST STATEMENT

Authors declare that there is no conflict of interest regarding the publication of this paper.

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