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Original Research Article

EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES OF METHYLENE BLUE DYE ADSORPTION FROM WASTEWATER USING MANILA TAMARIND SHELL COPPER NANOPARTICLES AS ADSORBENT

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ABSTRACT: The current study's objective is to use Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs as adsorbent in a batch process to remove Methylene Blue dye from their wastewater. Contact time, solution pH, initial Methylene blue dye concentration, adsorbent dosage, and temperature were the factors that were examined in batch research. The maximum removal efficiency was predicted to be 96.37% at a temperature of 318 K, a solution pH of 7, an initial dye concentration of 10 mg/L, and an adsorbent dosage of 0.5 g/L. The Freundlich isotherm model best describes Methylene Blue removal adsorption data at 303 K, with a correlation coefficient of 0.9975, while the Temkin and Langmuir isotherms have correlation coefficients of 0.8901 and 0.8656, respectively. The kinetics study analyzed adsorption data using pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion models. Pseudo-second-order kinetics for methylene blue showed close applicability, confirming chemisorption as the rate-limiting step. The pseudo-second-order kinetics model best describes Methylene Blue removal adsorption data at 10 mg/L with a correction coefficient of 0.9988, while the pseudo-first-order, Elovich model, and intra-particle diffusion model have correction coefficients of 0.9876, 0.9704, and 0.9174, respectively. The thermodynamic study found that the adsorption process is spontaneous and physisorption is dominant, with Gibbs free energy values ranging from -20 to 0 kJ/mol. Endothermic adsorption and an activated complex formation are associated with the process. In this study, determine the ΔH^0, ΔS^0, and ΔG^0 at 303K with values of 25.766 kJ/mol, 114.12 J/mol, and -8.800313299, respectively.

Key Words	Methylene blue, Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs), wastewater, Adsorption
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1.INTRODUCTION

Many times, around the world, freshwater is a restricted resource. Population growth, urbanization, and climate change will all contribute to increased scarcity. The main reason for the scarcity of fresh water is not only the high demand for water, but also contamination in a freshwater ecosystem. Human-caused contamination in this ecosystem has significantly reduced usable water and increased the expense of purifying it. The primary sources of water pollution are point and non-point sources. Point sources include pollutants discharged through pipelines, such as home sewage, and industrial waste effluents from industries or plants into receiving waters. It differs from non-point pollution caused by storm runoff, which spreads contaminating elements diffusely across land.

Manila tamarind shells, which are commonly thrown as agricultural waste, are high in bioactive components such tannins, flavonoids, and polyphenols. These chemicals can operate as natural reducing and stabilizing agents in the synthesis of copper nanoparticles, offering an environmentally benign and cost-effective method of nanoparticle production while supporting sustainable waste management.(Prasad *et al.*, 2023). Copper nanoparticles are known for their catalytic effectiveness and high surface reactivity, making them excellent candidates for eliminating methylene blue dye from wastewater. Their capacity to breakdown dye molecules efficiently, along with their cost-effectiveness, highlights their viability for environmental cleanup. The removal of methylene blue dye from wastewater is crucial to minimizing environmental contamination. Traditional adsorbents, such as activated carbon and clays, are commonly used for dye removal, but they have considerable disadvantages, including high cost, limited reusability, and environmental problems during production. While several alternatives have been investigated, few focus on sustainable, green materials that provide both high efficiency and little environmental impact. (Adewale Akintelu, S. *et al.,2021).*

The goal of this study is to create a green synthesis technique for copper nanoparticles that uses manila tamarind shells as a natural precursor. The produced CuNPs will be studied and tested for their ability to remove methylene blue dye from wastewater. This work provides a long-term solution to water contamination by combining agricultural waste utilization and color remediation techniques. The purpose of this study is to investigate the efficacy, cost-effectiveness, and environmental sustainability of MTS-CuNPs for removing methylene blue dye from wastewater. By resolving the limits of existing adsorbents, this study paves the way for a more sustainable approach to wastewater treatment.

NaIO4-CNP, a new adsorbent material derived from cotton fibers, effectively removes methylene blue dye from textile wastewater, demonstrating excellent reproducibility and potential for wastewater treatment (Melese and Tsade, 2024).Spirulina platensis biosorbs lead, cadmium, and nickel ions from aqueous solutions, with endothermic sorption and selectivity towards Pb2+ ions. Its reusability and capacity towards these metal ions are studied(Şeker *et al.*, 2008). Polyaniline with chitosan adsorbent for Acetaminophen removal achieved high adsorption rate, best fit by pseudo-second-order and Langmuir models, and retains 69% capacity after five cycles.(Daikh *et al.*, 2022). The study investigated lead biosorption using Tectona grandis L.f. biomass, analyzing factors like contact time, initial metal ion concentration, pH, adsorbent dosage, temperature, and adsorbent size. Results showed good adsorption capacity and spontaneous process.(Naidu *et al.*, 2013) This study investigates the use of genetically modified bacteria to address heavy metal pollution in water. Using Escherichia coli expressing human metallothioneins, the study found MT3 biosorbent as a promising method for Pb^{2+} biosorption, with a maximum capacity of 50mg $Pb^{2+}g^{-}$ and up to 74% recovery. (Akkurt *et al.*, 2024) The study explores the use of activated teak leaf powder as a biosorbent for Congo red dye removal from wastewater, revealing its potential as a cost-effective, environmentally friendly, and efficient method.(Gedam *et al.*, 2019) Research on fungal decolorization of dye wastewater explores mechanisms, elution and regeneration methods, pretreatment methods, and factors affecting decolorization(Fu and Viraraghavan, 2001).The study developed a Fe_3O_4/GO nanocomposite for efficient water treatment, demonstrating high adsorption capacity under optimal conditions like pH 6.0, 50.0 mg adsorbent weight, and 10 min contact time.(Cao *et al.*, 2024). The research evaluates the Langmuir Linear type 3 isotherm for optimal BG adsorption on MWCNTs, a low-cost, low-contact time adsorbent for dye removal.(Mahdi *et al.*, 2023).The study assessed adsorption and coagulation processes for removing reactive dyes Orange 16 and Black 5, using coconut-based PAC and alum chloride. Results showed Orange 16 had higher adsorption capacity(Lee *et al.*, 2006). The study demonstrates the preparation of activated carbons from walnut shells using zinc chloride, with the optimum carbon having a BET surface area of 1800 m^2/g and pore volume of 1.176 cm^3/g (Yang and Qiu, 2010). The study uses potato plant waste as an adsorbent to remove methylene blue and malachite green dyes from aqueous solutions, characterized using SEM and FTIR spectroscopy(Gupta, Kushwaha and Chattopadhyaya, 2016). Mordenite and nanocrystal effectively adsorb new methylene blue from aqueous solutions, with higher adsorption capacity. Adsorption kinetics follow pseudo second-order kinetics, with higher pH resulting in higher adsorption capacity(Sohrabnezhad and Pourahmad, 2010). A carbon-microsilica composite adsorbent was developed using microsilica, demonstrating effective cationic organic dye capture and methylene blue removal, with the Langmuir equation providing more accurate results(Zhang *et al.*, 2012). Gambir Indonesia was modified to remove methylene blue from aqueous solutions, with a adsorption capacity of 149.3 mg/g and a well-fit pseudo-second-order equation(Tong, Azraa and Noordin, 2012). The study investigates the use of agricultural waste-based bioadsorbents as cost-effective, biodegradable, and environmentally friendly alternatives to conventional adsorbents for removing methylene blue dye from wastewater(Sahoo and Kundu 2023). This review paper explores eco-friendly biosorbents for removing methylene blue from water bodies, highlighting their importance in green chemistry for wastewater treatment and environmental pollution mitigation (Saha, and Debnath 2023) The study explores the use of biodegradable green adsorbents from natural and renewable sources for efficient methylene blue removal from water solutions, demonstrating cost-effective, environmentally friendly, and high-efficiency alternatives (Singh and Sharma 2023). Using copper nanoparticles made from environmentally benign plant extracts, the study investigates green solutions for pollutant remediation, demonstrating their exceptional dye adsorption properties and promise for wastewater treatment.(Rani, S., and Paliwal, A. 2022)

2. MATERIALS AND METHODS

2.1 Preparing the dye solution:

1 g of 100% Methylene Blue dye was dissolved in 1000 mL of distilled water to make stock solutions with a concentration of 1000 mg/L. The solution was produced in standard flasks. These stock solutions were then diluted to the desired dye concentration (10-100 mg/L) by mixing with a suitable proportion of distilled water.(Umoren, Etim and Israel, 2013)

2.2 Chemicals and reagents:

Copper Sulphate Pentahydrate ($CuSO_4.5H_2O$) was used without additional purification after being purchased from Sigma Aldrich. Manila tamarind shells were gathered in Medak District's Narsapur jungle. Double-distilled water was used to make the plant extract and copper sulfate solution. The UV spectrophotometer, beakers, Eppendorf tubes, funnels, and falcon tubes were all sterile, as was the work area(Bulut and Aydın, 2006).

2.3 Preparation of Manila Tamarind Shell extract:

Manila Tamarind Shell samples were washed with distilled water and ground into fine pieces, then 20g of MTS powder was added to 100ml of double distilled water, mixed thoroughly, and cooked in a hot water bath for 45 minutes. The extract was then filtered through Whatman No.41 filter paper to provide Manila Tamarind shell aqueous extract, which was refrigerated for later use(Ravikumar and King, 2019).

2.4 Synthesis of Cu-NPs:

4 g of copper sulfate pentahydrate and 100 cc of Manila Tamarind shell aqueous extract were magnetically stirred at room temperature (27oC) for four hours. Within 10 minutes, the blue color of copper sulfate pentahydrate changed brown, indicating the formation of CuNPs due to the reduction of copper ions from Cu (II) ions to Cu metal. The samples were then centrifuged at 3000 rpm for 10 minutes, yielding a clear, room-temperature supernatant. Copper nanoparticles were dried in an oven at 80 to 90 degrees Celsius for four hours before being examined using FT-IR, SEM, and XRD(Adewale Akintelu *et al.*, 2021). The size of the particles are reported to be nano in size and are reported elsewhere (Dasari KiranKumar and Pulipati King, 2025).

2.5 Batch Mode Adsorption Studies:

Batch biosorption equilibrium studies were carried out in 250 mL conical flasks with a constant agitation speed (150 rpm). All studies were conducted at room temperature (±300C). The concentrations of both dyes before and after sorption were determined with a UV-Vis spectrophotometer by measuring the absorbance of the dye employed(Aksu, 2005)(Mall *et al.*, 2005)(Kiran *et al.*, 2006)(Sreelatha and Padmaja, 2008).

2.5.1 Effect of Contact Time:

By adding 0.5 g/L of 100 nm Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) to Erlenmeyer flasks holding 10 mg/L of Methylene Blue dye solution at pH 7 and temperature 303 K, the impact of contact length on dye biosorption was examined. This solution was centrifuged after being agitated for five minutes at 150 rpm. The supernatant was properly decanted after centrifugation, and the amount of remaining Methylene Blue dye was measured. At different intervals of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 minutes, the technique was repeated. This makes it possible to calculate the equilibrium time(Mall *et al.*, 2005).(Tsai *et al.*, 2006)

Table 1: Range of parameters covered.

Parameters	Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) adsorbent	
	Methylene blue	
	Min	Max
Contact time(t), min	5	100
Solution, pH	4	9
Adsorbent dosage (w), (g/L)	0.1	0.8

Initial dye concentration(C_0), (mg/L)	10	100
Temperature(T), (K)	303	318

2.5.2 Effect of Solution pH:

A known quantity of Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) was added to 100 mg/L of Methylene Blue dye solutions at varying concentrations (10, 20, 30, and 50 mg/L), each maintained at a different pH (4 to 9) and at 303K to ascertain the impact of solution pH on Methylene Blue dye biosorption. After agitating these solutions for an equilibrium period at 150 rpm, the concentrations of leftover dye were determined (Bulut and Aydın, 2006)(Salleh *et al.*, 2011).

2.5.3 Effect of Initial Dye Concentration:

By adjusting dye solution concentrations (Methylene Blue dye) between 10 mg/L and 100 mg/L, the impact of starting dye concentration on dye biosorption was investigated. A known weight (0.5 g/L) of Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) was added to solutions with varying Methylene Blue dye concentrations. After centrifuging and agitating these solutions for an equilibrium period at 303 K, the final dye concentrations were measured. Keeping all other factors equal, this process was carried out at various initial dye concentrations between 10 and 100 mg/L(Waranusantigul *et al.*, 2003)(Kavitha and Namasivayam, 2007).

2.5.4 Effect of Adsorbent Dosage:

By agitating 100ml of Methylene Blue solution with varying initial concentrations (10 to 50 mg/L) using 0.1, 0.2, 0.3, 0.4, and up to 0.8 g/L of Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as an adsorbent dosage at room temperature for equilibrium contact time and optimal pH at a constant speed of agitation, the effect of adsorbent dosage on the amount of dye adsorbed was ascertained. The concentrations of un-adsorbed dye were measured after these solutions were shaken for the equilibrium period. Keeping all other factors equal, this process was carried out with several concentrations of biosorbent (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 g/L)(Chakraborty, Chowdhury and Saha, 2012) (Gouamid, Ouahrani and Bensaci, 2013)

2.5.5 Effect of Temperature:

By stirring 0.5 g/L of Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) with varying quantities (10 mg/L to 50 mg/L) of Methylene Blue dye at 303 K and the ideal pH, the impact of temperature on dye removal was investigated. Solutions were taken out and their final dye concentrations were measured at the conclusion of the equilibrium period. This process was carried out again with comparable circumstances and at varying temperatures between 3030 and 3180 K(Anbia and Hariri, 2010).

3. RESULTS AND DISCUSSION

Manila tamarind shells, derived from Pithecellobium dulce, serve as a crucial natural reducing and capping agent in the conversion of copper sulfate ($CuSO_4$) into copper nanoparticles (CuNPs). The mechanism typically involves the following:

Reduction of Copper Ions: Manila tamarind shells contain various phytochemicals, such as polyphenols, flavonoids, and tannins. These chemicals have hydroxyl and other functional groups that serve as reducing agents.

- The Cu^{2+} ions in $CuSO_4$ are reduced to Cu^0 by the phytochemicals in an aqueous or suitable solvent medium.

$$Cu^{2+} + \text{Phytochemical} \rightarrow Cu^0 + \text{Oxidized Phytochemical}$$

Stabilisation (Capping): Once the copper ions have been converted to metallic copper (Cu), the same phytochemicals serve as capping agents. The capping technique avoids nanoparticle aggregation and keeps them stable in the colloidal phase.

Mechanism Details: Electrochemical mechanism: The electron-donating characteristics of functional groups such as hydroxyls (-OH) and carbonyls (-C=O) aid in electron transfer to Cu^{2+}, reducing it to Cu^0. (Muthuvel, A. and Jeyaraj, M., 2020).

3.1 Effect of Contact Time

Fig. 1 displays the percentage of adsorption that was measured at various contact times. According to the figure, the percentage of Methylene Blue dye removal grew sharply as contact time increased from 5 to 60 minutes. After reaching equilibrium for 60 minutes, the proportion of dye removal reached plateu. Consequently, given the experimental setup employed in this investigation, a contact time of 60 minutes is adequate for the removal of Methylene Blue dye. For an initial dye concentration of 10 mg/L, the percentage of Methylene Blue dye removed using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as an adsorbent increased from 60.49 to 92.01%, and the contact time increased from 5 to 100 minutes. With an increase in contact time from 5 to 60 minutes, the percentage of dye removal for 50 mg/L rose from 51 to 87.99% mg/g, respectively.

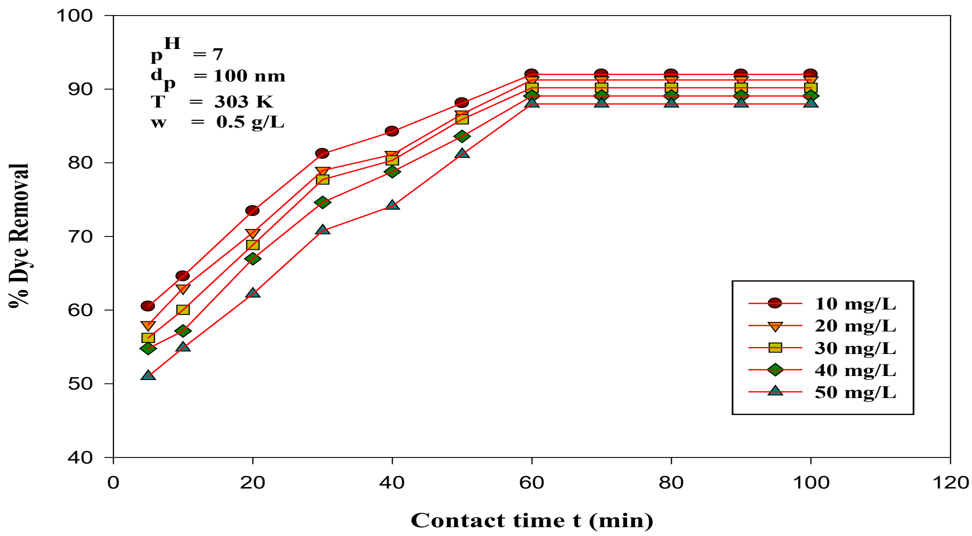

Fig. 1: Effect of Contact Time on % Dye Removal of Methylene blue Using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent.

3.2 Effect of Solution pH

One of the key regulating factors in the adsorption process is the pH of the solution. Using Fig. 2, the impact of solution pH on the percentage of dye removed for the removal of Methylene Blue dye was examined. At an initial concentration of 10 mg/L, it was found that the percentage of adsorption for Methylene Blue decreased from 44 to 64% as the pH of the solution increased from 2 to 6 and decreased when the pH of the solution increased from 6 to 9 for Methylene Blue. When the pH of the solution rose from 2 to 9, the percentage of adsorption for Methylene Blue increased from 36% to 58% at an initial concentration of 50 mg/L. The highest percentage of dye clearance was found at pH 6.

3.3 Effect of Initial Concentration of Dye

Fig. 3 illustrates how the initial dye concentration affects the percentage of dye removal. The figure clearly shows that when the original dye concentration increased from 10 to 100 mg/L, the percentage of dye removal declined. When the initial concentration of Methylene blue increased from 10 to 100 mg/L at 303 K, the percentage of dye removal of Methylene blue dropped from 94.80 to 88.16 percent.

3.4 Effect of Adsorbent Dosage

The outcome, which is displayed in Fig. 4, shows that when the dosage of adsorbent was increased, so did the percentage of dye removal. At an initial concentration of 10 mg/L of Methylene blue, the percentage of dye removal rose from 61.04 to 94.44% when the adsorbent dosage was raised from 0.1 to 0.8 g/L. The percentage of dye removal rose from 50.25 to 89.36% for an initial concentration of Methylene blue of 50 mg/L when the adsorbent dosage was raised from 0.1 to 0.8. g/L.

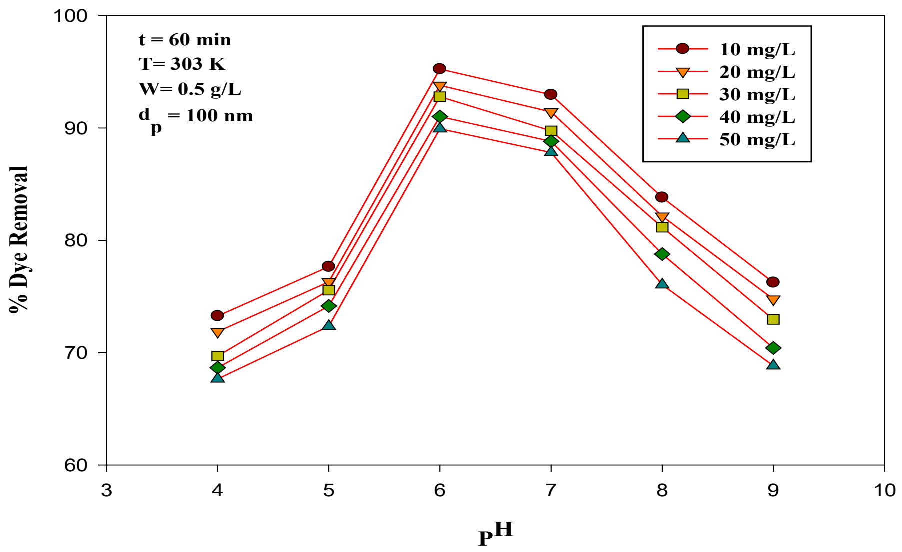

Fig. 2: Effect of Solution pH on % Dye Removal of Methylene blue Using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent

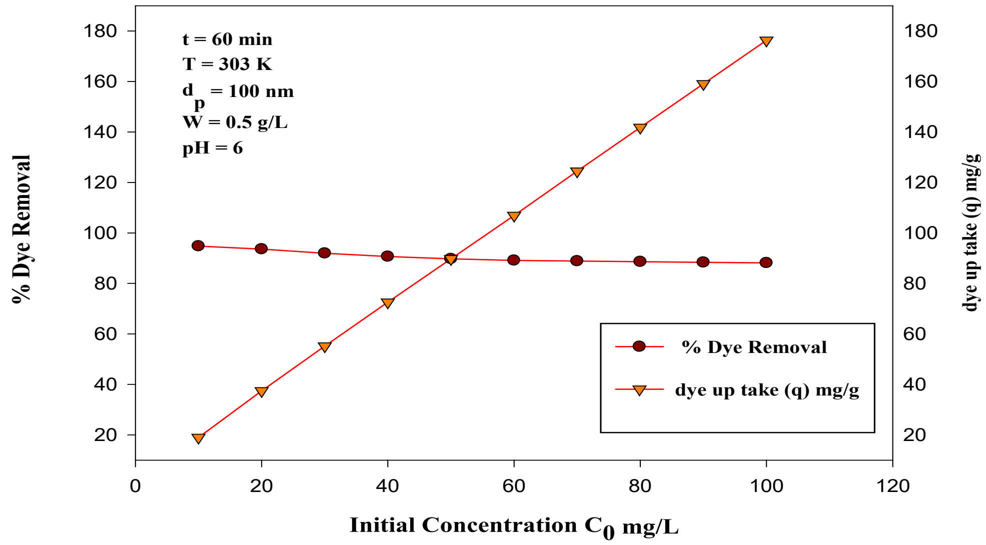

Fig. 3: Effect of initial concentration of Methylene blue on dye uptake and % dye removal using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs adsorbent.

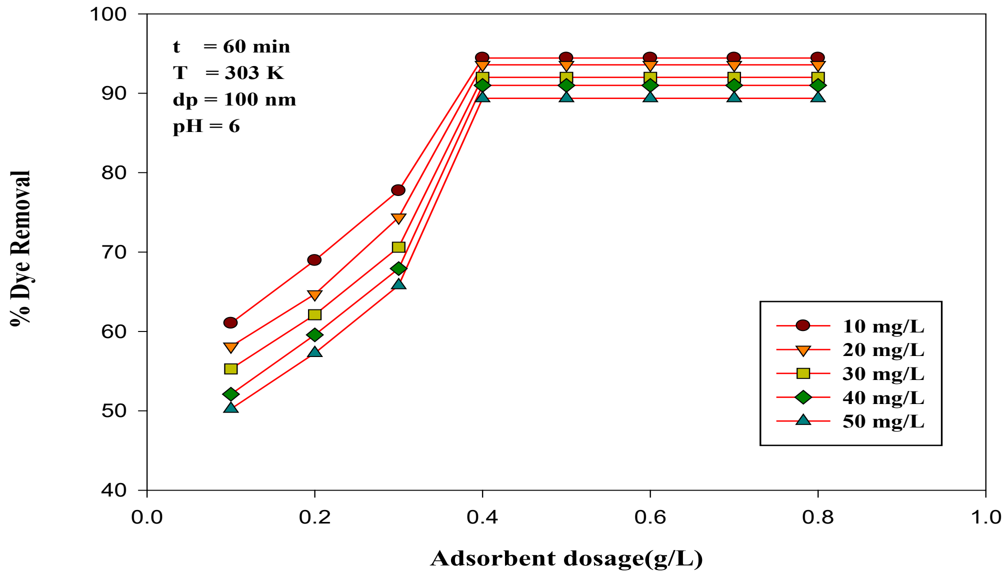

Fig. 4: Effect of adsorbent Dosage on % Dye removal of Methylene Blue Using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent

3.5 Effect of Temperature

The outcome is displayed in Fig. 5. The graphic showed that as the solution's temperature rose, so did the percentage of dye elimination. This implies that the adsorption process is endothermic. When the solution temperature was raised from 303 K to 318 K, the percentage of dye removal increased from 94.26 to 96.37% and 89.78 to 92.13% for initial concentrations of Methylene Blue dye of 10 mg/L and 50 mg/L, respectively.

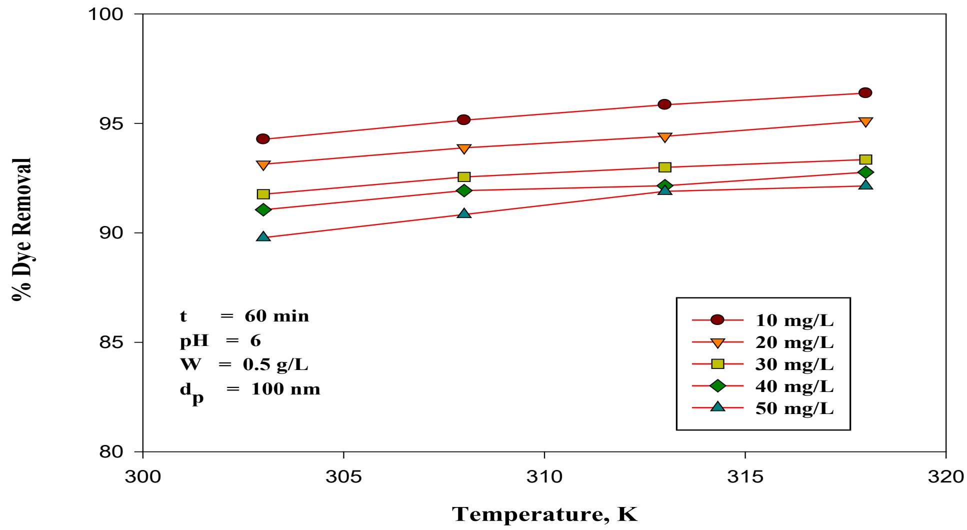

Fig. 5: Effect of temperature on % Dye Removal of Methylene blue using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent

3.6 Equilibrium Studies

3.6.1 Langmuir Adsorption Isotherm:

For the adsorption of Methylene blue at 303 K, the Langmuir plot (C_e/q_e vs C_e) is displayed in Fig. 6. The adsorption of Methylene blue dye onto Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent followed the Langmuir isotherm, correlation coefficient (R^2) was determined to be 0.8656. The slope and intercept of the linear plots of Ce/qe vs Ce for Methylene Blue were used to determine the parameters q_{max} and b. For Methylene blue, the highest adsorption capacity (q_{max}) and b values were 301.2 mg/g and 0.097 L/mg. Table 2 contains a tabulation of these values. A more accurate measure of adsorption is thought to be the R_L parameter. The separation factor R_L was computed at a concentration of 10 mg/L based on the values of b. As seen in Table 2, it was discovered that the R_L for Methylene blue was 0.5. These findings showed that Methylene blue had a preferential adsorption onto the adsorbent.

3.6.2 Freundlich Isotherm:

The slope and intercept of the graph of ln q_e vs ln C_e are used to determine the values of K_f and n. Fig. 7 displays the Freundlich curve (ln q_e against ln C_e) for Methylene Blue adsorption at 303 K. The plot revealed that the 1/n value and the K_f value for Methylene blue was 0.698 & 29.964 ((mg/g)/(L/g) n). The findings showed that the 1/n value ranged from 0 to 1, indicating that Methylene blue's adsorption onto Manila Tamarind Shell Copper Nanoparticles (MTS-Cu-NPs) was advantageous under the conditions under investigation. This could be because of the chemical interactions between the adsorbent and the adsorbate. The correlation coefficient R^2, which was used to examine the data, was determined to be 0.9975 for Methylene Blue. These findings showed that the Freundlich model fit the methylene blue adsorption data quite well.

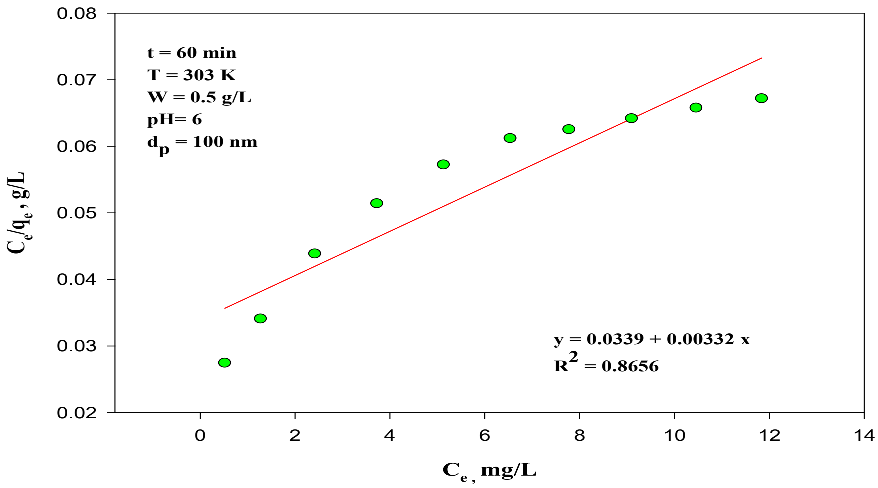

Fig. 6: Langmuir Isotherm for Adsorption of Methylene blue dye using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent

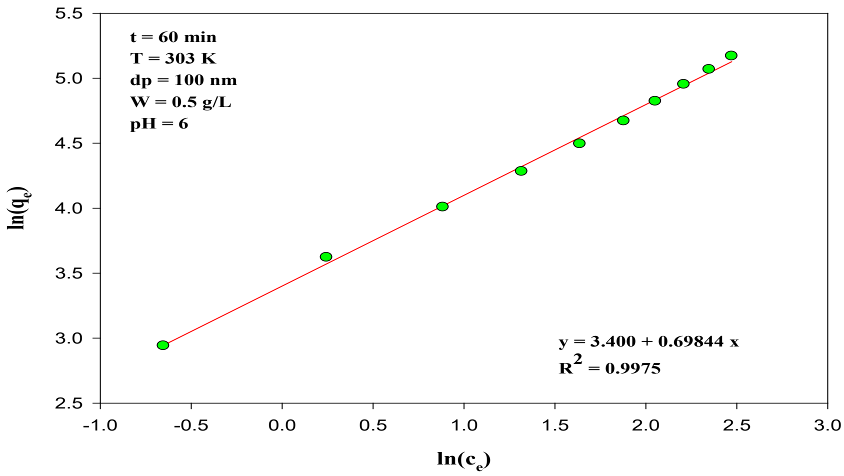

Fig. 7: Freundlich Isotherm for Adsorption of Methylene blue using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent.

3.6.3 Temkin Isotherm:

A plot of q_e versus lnC_e enables the determination of the isotherm constants A_T and b_T. Fig. 8 shows the linear plot of qe versus lnCe for Methylene blue adsorption on to the Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent and the values of the parameters are given in Table-2. The correlation coefficient (R^2) value was determined is 0.8901. the determination of the isotherm constants A_T and b_T valves in Table 2.

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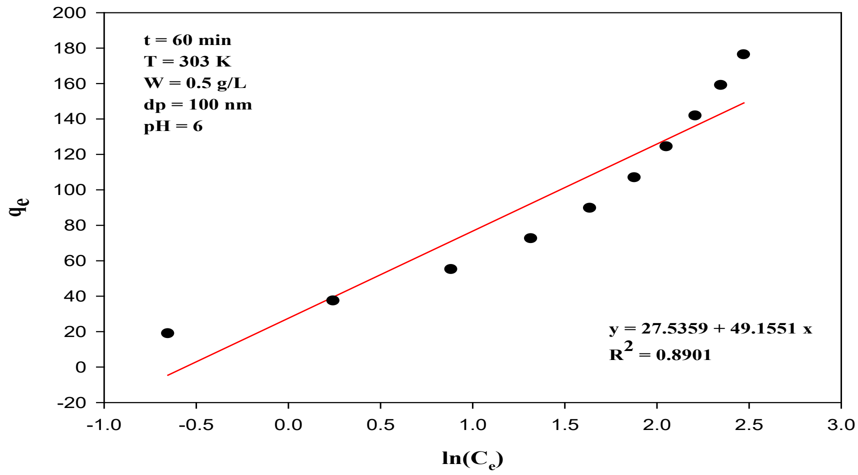

Fig. 8: Temkin Isotherm for Adsorption of Methylene blue using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent.

All three of the models under study examined the equilibrium data. The high correlation coefficient R^2 values shown in Table 2 were used to identify the best fit isotherm model. Based on these R^2 values, it was determined that, at a solution temperature of 303 K, the Freundlich isotherm model, which had a correlation coefficient of 0.9975, best described the adsorption data for Methylene Blue Removal. Temkin and Langmuir isotherms, on the other hand, had correlation coefficients of 0.8901 and 0.8656, respectively.

Table 2: Adsorption Isotherm Constants for dye Removal Using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) Adsorbent.

Name of the isotherm model	Constants	Methylene Blue
Langmuir	b(L/mg)	0.097
	q_{max} (mg/g)	301.2
	R_L	0.5
	R^2	0.8656
Freundlich	k_f(mg1-1/nL1/1g-1)	29.964
	n	1.4317
	R^2	0.9975
Temkin	A_T (Lg-1)	1.7509
	b_T (J mol-1)	49.1551
	R^2	0.8901

High correlation coefficient, R^2, values suggest that the Adsorption process could be due to homogeneous surface coverage. This is in good agreement with the result of Freundlich Isotherm for Methylene blue dye.

Data comparing biosorption capabilities (q_{max}) for Methylene blue:

Adsorbent	q_{max} (mg/g)	Reference
Wheat shells	16.56	Bulut and Aydin (2006)

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Egg shell	16.43	Sharma et al. (2009)
Neem leaf powder	3.67	Bhattacharyya and Sharma (2005)
Indian rose wood saw dust	11.8	Garg et al. (2004)
Fly ash	1.91	Sahaand Datta (2009)
Coconut coir	15.59	Tsai et al. (2006)
Orange peel	18.6	Annadurai et al. (2002)
MTS-Cu-NPS	301.2	Present study

3.7 Kinetic Studies

3.7.1 Pseudo- First-Order Kinetic Model:

The pseudo-first order kinetic model for the adsorption of Methylene blue was evaluated at various initial concentrations (10 to 50 mg/L) using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) show in Fig. 9. The linear plot of ln(q_e-q) versus t was used to calculate the equilibrium adsorption capacity and first order rate constant values, which were then Table-3 with the correlation coefficient (R^2) values for Methylene blue. The correlation coefficient values of Methylene blue, despite being highly high, did not align with the computed and experimental qe values, indicating that the first-order kinetics of Methylene Blue's adsorption onto MTS-CuNPs were not followed.

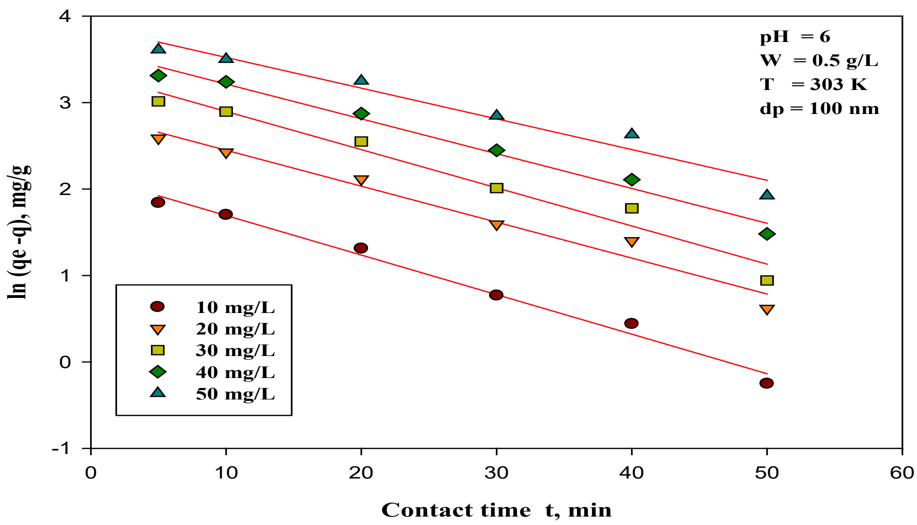

Fig. 9: Pseudo First Order Kinetic Model for Methylene blue dye using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as Adsorbent.

3.7.2 Pseudo-Second-Order Kinetic Model:

Plots of t/q vs. t were used to independently assess the validity of the pseudo-second order kinetic model for the adsorption of Methylene Blue utilizing Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as an adsorbent. Figs. 10 display these plots. The equilibrium adsorption capacity and second order rate values are obtained from the slope and intercept of the linear plot and are listed in Tables -3 along with the R^2 values. These findings imply that the pseudo-second order model can be applied to the experimental data. Both physisorption and chemisorption are present, according to the pseudo second order kinetic model's applicability.

3.7.3 Elovich Kinetic Model:

The slope and intercept of the straight-line plot of q vs. ln t in Figure 11 are used to determine the constants. Table 3 provides a summary of the Elovich equation results acquired for the adsorption of Methylene Blue onto Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) in this investigation. For Methylene Blue dye, the correlation coefficients for the Elvovich equation varied between 0.9517-0.9704, respectively. Low correlation coefficient values were discovered, indicating that the Elvovich model is not understandable in respect to the experimental data.

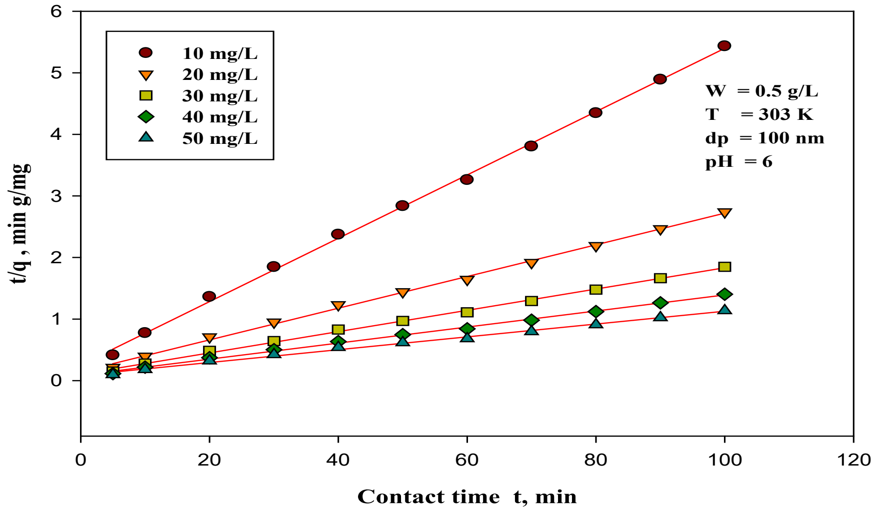

Fig. 10: Pseudo Second Order Kinetic Model for Methylene blue using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) Adsorbent.

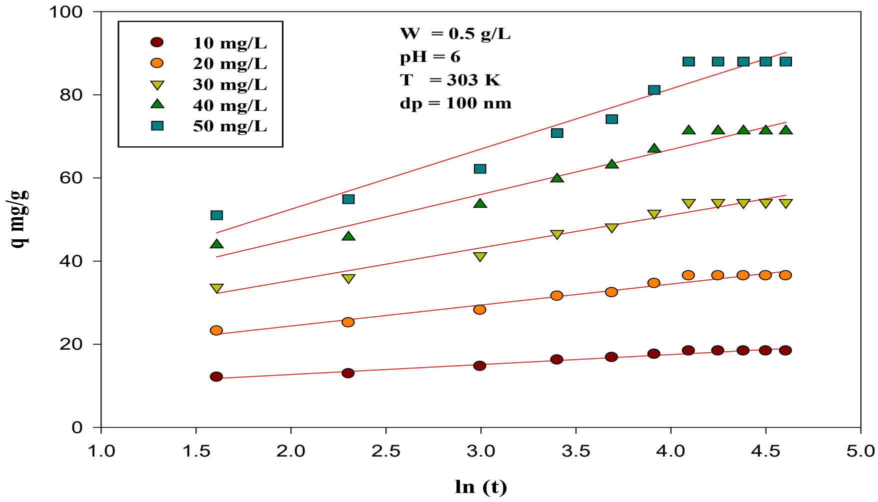

Fig. 11 Elovich model Kinetic Model for Methylene blue using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) Adsorbent.

3.7.4 Intra-particle diffusion Kinetic Model:

The computed intra-particle diffusion rate constant K_{id} values for methylene blue are displayed in Table 3.

Furthermore, the fact that the intra-particle diffusion region's straight line did not pass through the origin in Fig. 12 suggests that the intra-particle diffusion was not the only step that limited the rate. The substantial boundary layer effect on the adsorption process is indicated by the high intercept values. Therefore, the current adsorption process may be primarily regulated by the surface adsorption mechanism in conjunction with intra-particle diffusion.

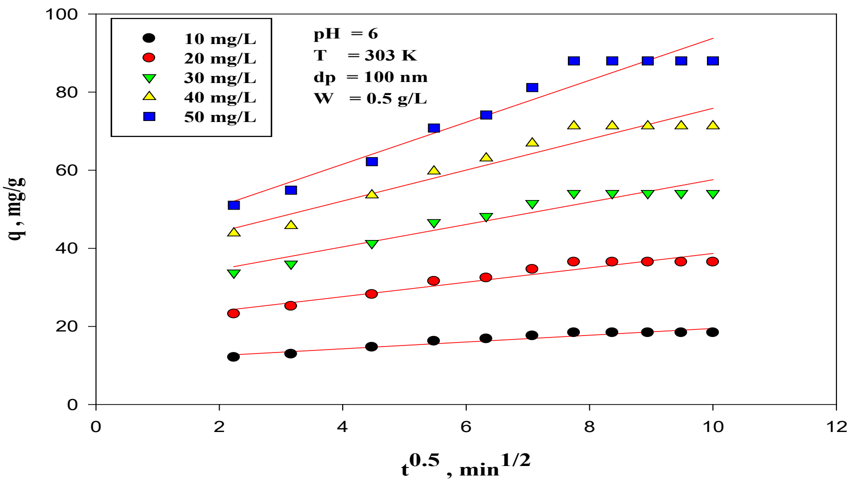

Fig.12: Intra-particle diffusion model Kinetis model for methylene blue dye using Manila Tamarind shell Copper Nanoparticles (MTS-CuNPs)

The study analyzed adsorption data using pseudo-first order, pseudo-second order, Elovich, and Intra-particle diffusion models. The results showed that the theoretical qe values from the first order kinetic model and Elovich model were significantly different from experimental values, and the correlation coefficients were lower. The pseudo-first order kinetic model, Elovich model, and Intra-particle diffusion model did not accurately describe the sorption system. However, the calculated qe values were close to the experimental qe values and the correlation coefficients were close to unity for pseudo-second-order kinetics for Methylene blue. The applicability of pseudo-second order kinetic model results confirmed that the rate limiting step in the process is chemisorption.

3.8 Thermodynamic Studies

Thermodynamic studies provide information about the feasibility of the process and the nature of the adsorption process. In order to estimate the thermodynamic parameters for the adsorption of Methylene blue dye using *Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs)* as adsorbent, the experiments were conducted, and data were analyzed. The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear Van't Hoff plot i.e ln (q_e/c_e) vs (1/T). These plots are shown in Fig. 13 for Methylene blue dye. The estimated thermodynamics properties along with the correlation coefficients (R^2) are tabulated in Table 4. The adsorption process of Methylene blue using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) was studied using various parameters. The negative value of ΔG^0 at a given temperature confirmed the spontaneous nature of the adsorption process, while the decrease in ΔG^0 values with temperature indicated a decrease in adsorption feasibility. The physisorption mechanism was found to be dominant, with Gibbs free energy values ranging from -20 to 0 kJ/mol. The positive value of ΔH^0 indicates endothermic adsorption, as the total energy absorbed in bond breaking is more than the energy released in bond making. The positive value of ΔS° suggests that the adsorption leads to order through the formation of an activated complex, suggesting an associated mechanism.

Van 't Hoff Equation: $\ln Kc = -\Delta H/ R\, T + \Delta S/ R$

Where: ln Kc: Equilibrium constant at a given temperature.

T: Absolute temperature (K). R: Universal gas constant (8.314 J mol−1K)

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
$$\Delta G^0 = -RT \ln Kc$$

Table 3: Kinetic model parameters for Methylene blue removal using MTS coper nano particles (MTS-Cu-NPs).

Concentration, mg/L	Pseudo-first order kinetics			Pseudo-second order kinetics		
	$K_{1,ad}$ (1/min)	q_e (mg/g)	R^2	$K_{2,ad}$ g/(mg.min)	q_e (mg/g)	R^2
10	0.0457	8.5906	0.9876	0.0103	19.4552	0.9988
20	0.0415	17.535	0.9703	0.0044688	38.9105	0.998
30	0.0441	28.2022	0.9685	0.002853	57.8703	0.99798
40	0.0402	37.1996	0.9831	0.001923	76.923	0.99737
50	0.0355	48.2984	0.9607	0.001247	96.1538	0.99483
Concentration, mg/L	Elovich model			Intra-particle diffusion model		
	γ (g/mg)	α mg/(g.min)	R^2	K_{id}	I	R^2
10	0.4165	64.7808	0.97044	0.8691062	10.79435	0.91736
20	0.19786	85.0536	0.96926	1.8441901	20.23917	0.931
30	0.1271	94.7596	0.96572	2.8672991	28.89434	0.92546
40	0.0926	96.8221	0.96144	3.9588287	36.26327	0.9339
50	0.0691	73.4276	0.9517	5.3714315	40.03729	0.94487

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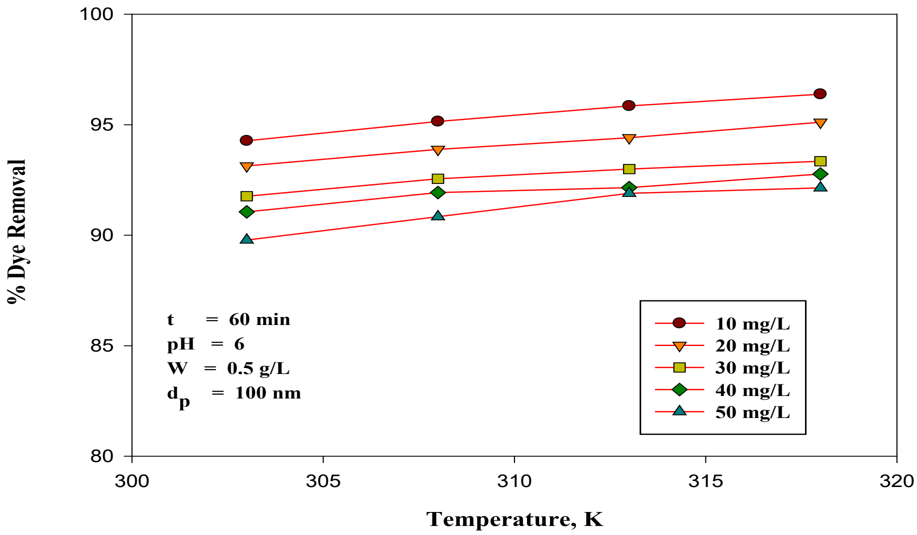

Fig. 13: Van't Hoff Plot for the Determination of Thermodynamic Parameters for the adsorption of Methylene blue dye by using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent.

Table 4: Thermodynamic Parameters for the Adsorption of Methylene blue dye using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as Adsorbent

Temperature, K	Methylene Blue		
	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)
303	-8.800313299	25.766	114.12
308	-9.395636191		
313	-9.974746926		
318	-10.50802723		

4. CONCLUSION

The data obtained from the Adsorption studies showed that a contact time of 60 min was sufficient for the maximum removal of Methylene blue dye from aqueous solution using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent.The experimental data of adsorption of the Methylene blue dye onto the Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) adsorbent fitted well with the Freundlich isotherm model. The isotherm reveals that the Adsorption of the dye onto Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) as adsorbent was favorable. The maximum removal efficiency was predicted to be 96.37% at a temperature of 318 K, solution pH of 7, and initial dye concentration of 10 mg/L and adsorbent dosage of 0.5 g/L. The experimental data of adsorption of the Methylene blue dye onto the Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) adsorbent fitted well with the pseudo-second order kinetic model results confirmed that the rate limiting step in the process is chemisorption. The adsorption process of Methylene blue using Manila Tamarind Shell Copper Nanoparticles (MTS-CuNPs) was studied using various parameters. The negative value of ΔG^0 at a given temperature confirmed the spontaneous nature of the adsorption process, while the decrease in ΔG^0 values with temperature indicated a decrease in adsorption feasibility. The physisorption mechanism was found to be dominant, with Gibbs free energy values ranging from -20 to 0 kJ/mol. The positive value of ΔH^0 indicates endothermic adsorption, as the total energy absorbed in bond breaking is more than the energy released in bond making. The positive value of $\Delta S°$ suggests that the adsorption leads to order through the formation of an activated complex, suggesting an associated mechanism. MTS-CuNPs are useful materials in a variety of industries, including water treatment, catalysis, antimicrobials, and electronics. They are cost-effective because they use agricultural waste as a precursor and employ a green synthesis process. Their recyclability and low operating costs make them economically feasible. MTS-CuNPs are scalable for industrial applications because of their facile, low-energy synthesis technique and readily available raw ingredients. Their ease of integration into current systems, as well as the growing need for sustainable technology, increases their potential for large-scale production.

AUTHOR CONTRIBUTIONS

Dasari Kiran Kumar: Writing (Original Draft and Review & Editing), Methodology, Conceptualization, Investigation, Data Curation, Resources

P King: Supervision, Review & Editing

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CONFLICT OF INTERESTS

There is no conflict of interest, according to the authors.

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