

Kinetic study of Methylene blue dye adsorption on *Neolamarckiacadamba* leaves

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Abstract

Biosorbent synthesized from mature leaves of Kadam (*Neolamarckiacadamba*) tree was utilized to expel a cationic dye, Methylene blue from simulated wastewater. Batch adsorption studies were investigated using four operational parameters: initial dye concentration, contact time, pH and adsorbent dose. The results inferred that 0.4 g/L biosorbent was proficient in removal of 10 mg/L dye solution at pH 4 when agitated for 30 minutes at 120 rpm. Isothermal behaviour was evaluated using different models like Langmuir, Freundlich and Temkin models. Adsorption kinetics was established by using various models like pseudo first-order, pseudo second-order and Elovich models. The experimental data was fitted well by Temkin isotherm. Adsorption kinetic data best fitted the pseudo second-order model. The results found out from this study concluded that KLP can be used as a cost-effective adsorbent in potential practical applications for dye removal from wastewater to abate colour pollution.

Keywords: *Neolamarckiacadamba*, biosorbent, Methylene blue, cost-effective, isotherm.

Date of Submission: 24-09-2022

Date of Acceptance: 08-10-2022

I. Introduction

The world is currently facing one of the most serious catastrophes i.e., water scarcity and this necessitates the potent utilization of available water resources. The exponential growth in global population and industrial development has remarkably affected water quality resulting in an increased global freshwater crisis. Various industries such as plastic, dye, textile, dyestuffs, paper, rubber, food, leather, cosmetics, carpet and printing use dyes in a large scale. Such industries utilizing dyes release dye effluents which have harmful effects upon living organisms and the environment. The disposal of dye-containing effluent into natural water bodies without proper treatment has an adverse effect on the photosynthetic activity in aquatic ecosystems (Nasar and Mashkoo, 2019). The coloured effluents disrupt the aesthetic nature of the water bodies thereby influencing the light permeability of the water surface. Consequently, the photosynthetic activity of the aquatic organisms is pestered leading to an imbalance in the aquatic ecosystem. Such effluents can lead to mutagenic or teratogenic effects on fish species and other aquatic biota owing to the presence of metals (Deering et al., 2020) and aromatics (Von Lau et al., 2014). Most of the synthetic dyes having aromatic nature are very stable and resistant to biodegradation as well as photo-degradation, thereby resulting in enduring water pollution (Mia et al., 2019; Berradi et al., 2019). Further, the existence of dyes in the environment has mild to severe toxic effects on human health, including carcinogenic, mutagenic, allergic and dermatitis effects, kidney disease, etc. (Lellis et al., 2019). The treatment of dyes becomes imperative since even a concentration as low as 1.0 mg/L in drinking water can impart intense colour to the water making it unsuitable for human consumption (Adegoke and Bello, 2015). Hence, existence of dyes in the water bodies has become a matter of grave concern. Owing to its negative impacts, dye wastewater should be properly treated prior to discharge into the environment.

Methylene blue (MB) is the most commonly used substance for dyeing cotton, wool and silk. Although MB is not considered as acutely toxic yet it can have various harmful effects. The marine pollution of MB is reported to exert abnormal metabolism, morphological deterioration and other dysfunctions. MB pose to be a bio-recalcitrance compound with negative effect on the ecology and environment, the intermediates formed after MB cleavage have adverse toxicity than their parent compound (de Oliveira et al., 2016; Santoso et al., 2020).

Since, plant leaves are a widely distributed natural resource and own the merits of low-cost, easy availability and renewable nature, leaves of Kadam (*Neolamarckiacadamba*) have been selected as adsorbent in the current study. Kadam tree is an evergreen, tropical tree native to South and Southeast Asia. The fresh leaves of this tree are usually fed to cattle. Apart from phytochemical studies no such reported work has been done so far upon *N. cadamba* tree leaves. Although, the leaf extract has recently been used to produce silver nanoparticles for surface-enhanced Raman spectroscopy.

Henceforth, this research paper intends to explore the feasibility to use the leaves of *N. cadamba* as a source of biosorbent to remove MB dye from waste suspensions without imposing any chemical stimulant/treatment.

II. Experimental Procedure

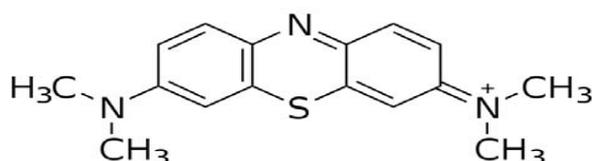
2.1 Adsorbate and biosorbent

Kadam tree leaves were collected from the University campus and thoroughly washed with distilled water to eliminate the impurities (dust and other water-soluble substances). The leaves were shade dried first at room temperature and then in a hot air oven at 105°C for 6 hours. The leaves were then crushed to fine powder and the resulting material was sieved to 100 μ size. The biosorbent was ready for use and stored in a plastic bottle in desiccator for further use.

A stock solution of MB was prepared by dissolving 1 g of dye in 1000 ml distilled water to make a stock solution of 1000 mg/L. Then, the experimental solution was prepared by diluting a definite volume of the stock solution to get the desired concentration. The batch sorption experiments were carried out in 250 ml Erlenmeyer flasks. The mixture was agitated at 120 rpm at room temperature. MB concentration was determined using a uv-visible spectrophotometer at 665 nm of adsorbance wavelength (λ_{max}). Final concentrations of the dye solutions were obtained from the standard calibration curve.

C.I. number	= 52015
C.I. name	= Basic blue 9
λ_{max}	= 665 nm
Empirical formula	= C ₁₆ H ₁₈ ClN ₃ S.3H ₂ O

Structure,



2.2 Batch biosorption experiments

Batch adsorption experiments were performed to evaluate the adsorption capacity of KLP for Methylene blue dye. Desired amount of synthesized biosorbent was added in 100 ml of aqueous solution of MB dye having a specific concentration and at the desired pH value. The pH of the dye solution was adjusted to the required value by adding 1 N HCl and/ or 1 N NaOH as required for pH adjustment. The dye solutions were then agitated at a constant speed of 120 rpm. The effect of operating parameters like pH of dye solution (2-10), contact time (0-90 minutes), initial dye concentration (10-70 mg/L) and adsorbent dose (0.1-0.6 g) on the extent of dye removal have been investigated. Samples were withdrawn from the shaker at specific time intervals, filtered and then centrifuged for 10 minutes at 4000 rpm. Finally, the residual dye concentration in the solution was analysed using uv-visible spectrophotometer at particular wavelength corresponding to the λ_{max} value of the dye.

The amount of MB dye uptake and percentage removal at equilibrium were calculated by using the following equations:

$$q_e = \frac{(C_i - C_f)}{W} \times V \quad (1)$$

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where, C_i = Initial Concentration (mg/L), C_f = Final Concentration (mg/L), V is the volume of solution (L), W is the mass of adsorbent (g) and q_e is the amount of dye adsorbed (mg/g).

2.3 Isothermal investigation of MB biosorption onto KLP

In order to understand the nature of the interaction between adsorbate and the adsorbent used for the removal of organic pollutants, adsorption isotherms are important (Aksu, 2005). The adsorption isotherm specifies the distribution of the adsorption molecules between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model isotherm that can be used for design purpose (El-Guendi, 1991). Adsorption isotherm is primarily important to describe the interaction of solutes with adsorbents and is crucial in optimizing the use of adsorbents. The values of the correlation coefficients, R² are judged and compared to ascertain the applicability of the isotherm equation.

In order to have an insight into the adsorption behaviours of Methylene blue dye onto Kadam leaf powder and to gain the optimal fitting of theoretical model, the experimental data from batch experiment were analyzed using Langmuir, Freundlich and Temkin isotherm equations in which linear regression analysis was used to evaluate whether the theoretical models have better or worse fit for the experimental data.

MB concentrations at equilibria (C_e) were quantified and the biosorption mechanisms were elucidated using established biosorption non-linear isotherms: Langmuir, Freundlich and Temkin (Freundlich, 1906; Langmuir, 1918).

Langmuir equation:
$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (3)$$

Freundlich equation:
$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

Temkin equation:
$$q_e = B_T \log A_T + B_T \log C_e \quad (5)$$

Adsorption kinetics is very important since it provides information regarding adsorption mechanism, process efficiency and its applicability on an industrial scale (Postai et al., 2016; Setiabudi et al., 2016; Wakkel et al., 2019).

Pseudo first-order model is based on the mechanism that occupation rate of adsorption sites is proportional to quantum of free sites available for the adsorption. The biosorption kinetics was investigated using the non-linear form of pseudo-first order kinetics as given by Eq. (6) :

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where, q_t and q_e are dye concentration at equilibrium and at time t (mg/g), and k_1 is the rate constant for pseudo-first order kinetics.

Pseudo second-order model is based on the principle that rate of occupation of adsorption sites is proportional to the square of amount of the free sites. Pseudo-second order kinetics (Ho, 2006) was determined by:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (7)$$

where, k_2 is the rate constant of pseudo-second order adsorption (g/mg min).

Thirdly, linearized Elovich equation (Low, 1960) was used for experimental data fitting and the relation is expressed as Eq (8):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (8)$$

where, α and β are kinetic constants.

III. RESULTS AND DISCUSSION

3.1MB biosorption onto KLP

Effect of initial dye concentration on MB adsorption

The removal efficiency was observed to be higher in case of lower MB dye concentration i.e., at an initial dye concentration of 10 mg/L as shown in Fig.1. However, at higher concentration the removal percentage continued to decrease and this might be due to increased driving force due to the concentration gradient (Kumar et al., 2011). Higher extent of dye removal at lower MB dye concentration can be attributed to maximum probability of binding of all molecules of dye to the biosorption sites at lower concentration, which cannot be the case for higher MB dye concentration as the available sites are fixed (Chowdhury et al., 2011).

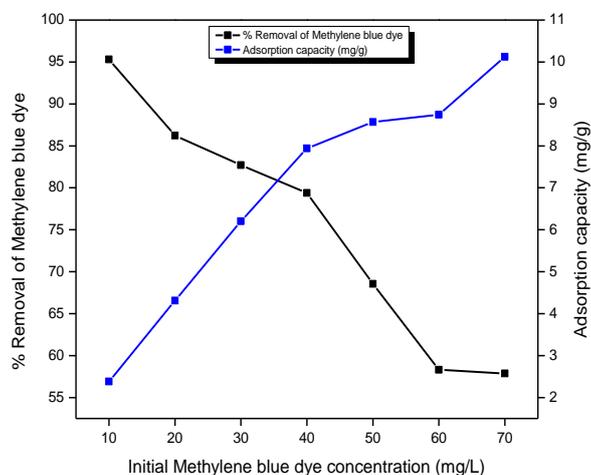


Figure 1: Effect of initial dye concentration on Methylene blue biosorption onto KLP
Effect of adsorbent dosage on MB adsorption

The increase in dye removal with biosorbent dosage till the optimum can be due to easy accessibility of a greater number of vacant sites at higher dosage on the biosorbent surfaces (Gündüz and Bayrak 2017). The highest percentage of dye removal was observed at an adsorbent dose of 0.4 g. Beyond that, there was no significant increase in the removal and instead it started declining. After the optimum biosorbent dosage, the variation in removal efficiencies can be attributed to aggregation of particles occurring at higher biosorbent dosage causing a decrease in biosorbent surface area (Ozacar and AyhanSengil, 2005).

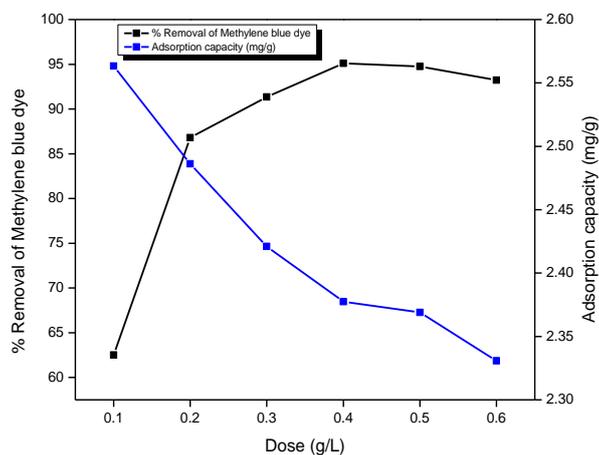


Figure 2: Effect of adsorbent dose on Methylene blue dye biosorption onto KLP

Effect of contact time on MB adsorption

The percentage removal of dye increased with the gradual increase in contact time. The maximum dye removal in initial periods is due to availability of maximum number of active sites for adsorption. The biosorption process was found to attain equilibrium at a contact time of 30 minutes. After that, even though the contact time was increased, the increase in dye removal percentage was quite insignificant. The dye removal after equilibrium slows down gradually due to reduction in the available sites for adsorption based on the occupancy. Aggregation of MB dye molecules with the increase in contact time blocks the active sites on KLP's surface which resists diffusion (Arfi et al., 2017).

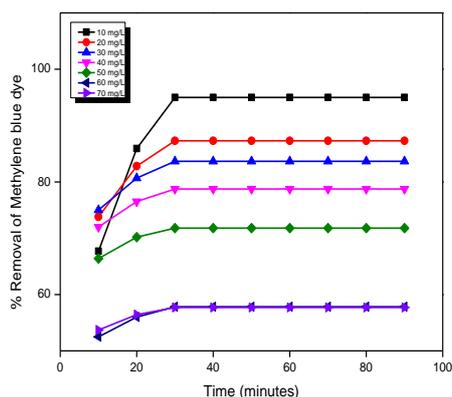


Figure 3: Effect of contact time on Methylene blue dye biosorption onto KLP

Effect of pH on MB adsorption

pH of the solution has a profound influence on adsorption process; it determines both the extent of adsorption of the dye molecule and the surface charge of the adsorbent. The adsorption of organic species is significantly influenced by the solution pH because pH governs the properties of adsorbent and adsorbate molecules such as the surface charge of the adsorbent and ionization degree of the adsorbate molecule (Ozturk and Silah, 2020; Putri et al.,2020; Singh and Dawa, 2014). The effect of pH on the uptake of MB dye was

investigated and the highest percentage of MB dye adsorbed was observed at pH 4. A gradual decrease was observed above pH of 4.

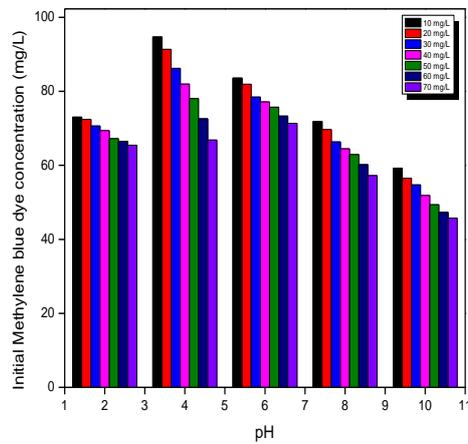


Figure 4: Effect of pH on Methylene blue dye biosorption onto KLP

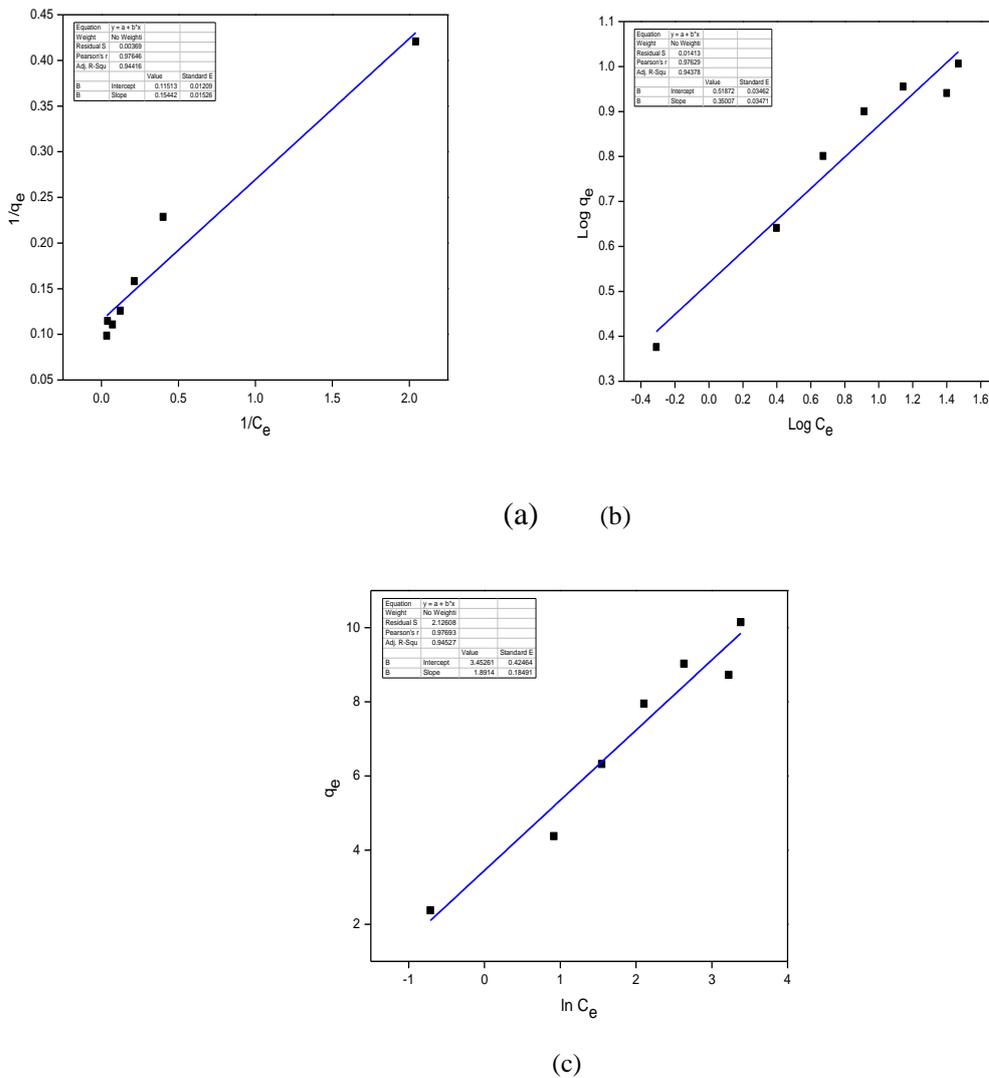


Figure 5:(a) Langmuir, (b) Freundlich, and (c) Temkin adsorption Isotherms

Table 1: Isotherm parameters for biosorption of Methylene blue dye on KLP

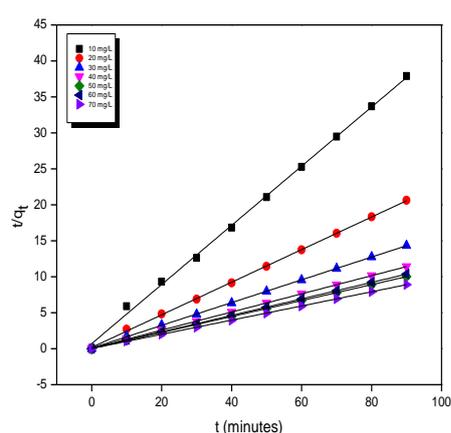
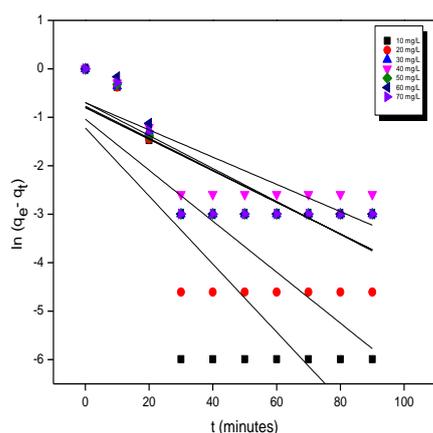
LANGMUIR ISOTHERM					
Intercept	Slope	q_m / q_{max} (mg/g)	K_L	R_L	R^2
0.11513	0.15442	8.68	0.75	0.12	0.94416
FREUNDLICH ISOTHERM					
Intercept	Slope	R^2	N	K_F	
0.51872	0.35007	0.94378	2.86	3.30	
TEMKIN ISOTHERM					
Intercept	Slope	R^2	B_T (J mol ⁻¹)	A_T (L mg ⁻¹)	
3.45261	1.8914	0.94527	1.89	6.21	

3.2MB biosorption equilibrium

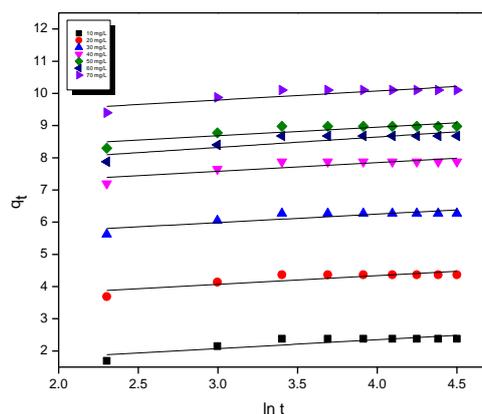
The equilibrium adsorption isotherm provides basic information in explaining the interactive behaviour between a sorbate and a sorbent, which is important in the design and analysis of sorption systems (Maurya et al.,2006; Namasivayam and Sureshkumar, 2008).

The linearized Langmuir, Freundlich and Temkin isotherm plots for the adsorption of Methylene dye by the KLP adsorbent are shown in Figs.5 (a,b and c) respectively. The results of the model parameters obtained from regressive analysis of these plots are presented in Table 1. It shows that the best fitted isotherm model is Temkin isotherm model. From Table 1, the highest value of the regression coefficient ($R^2 = 0.94527$) was found in the Temkin model, compared with the Langmuir ($R^2 = 0.94416$) and Freundlich ($R^2 = 0.94378$) models. Although the differences between the R^2 values of the three models is very less, Temkin adsorption isotherm model has to be considered the best fit. The Temkin isotherm model is derived assuming that with coverage there is a linear decline in the heat of adsorption unlike Freundlich isotherm which implies a logarithmic decrease in the adsorption heat (Krishna and Siva Krishna, 2013). The Temkin isotherm model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The maximum adsorption capacity of the adsorbent (q_{max}) was estimated to be 8.68 mg/g. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$) and irreversible ($R_L = 0$). The R_L (separation factor) value fell in the range of 0-1 and this suggests that the adsorption process is favorable. The value of Freundlich constant, n (2.86) is in between 1 and 10 which again proved that the adsorption is favorable.

3.3 MB biosorption kinetics



(a) (b)



(c)

Figure 6 : (a) Pseudo first-order, (b) Pseudo second-order and (c) Elovich kinetics models for biosorption of Methylene blue dye on KLP

Table 2 : Parameters of Pseudo 2nd order kinetics model for biosorption of Methylene blue dye onto KLP

Dye	Parameters	10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L	60 mg/L	70 mg/L
Methylene blue	$q_{e, cal}$ (mg/g)	2.43	4.41	6.32	7.92	9.02	8.73	10.15
	k_2 ($g\ mg^{-1}\ min^{-1}$)	0.24	0.28	0.31	0.31	0.32	0.25	0.30
	$q_{e, exp}$ (mg/g)	2.38	4.38	6.33	7.95	9.03	8.73	10.15
	R^2	0.99823	0.99963	0.99985	0.9999	0.99993	0.99988	0.99994

In order to select optimum operating conditions for the process design, the kinetics of adsorbate uptake is quite important. The adsorption data were analyzed using various models like pseudo first-order, pseudo second-order and Elovich kinetic models. The R^2 values of pseudo first-order deviate from unity while those of pseudo second-order model were very close to unity. Comparing the R^2 values obtained in the adsorption process, the suitability of the kinetic models for the adsorption data follows the order: pseudo second-order > Elovich > pseudo first-order. Besides, the amount of Methylene blue adsorbed per unit mass $q_{e, cal}$ (mg/g) determined from pseudo second-order model was found to be closer to $q_{e, exp}$ i.e., experimentally obtained. The results suggest that a heterogeneous adsorption mechanism is likely to be responsible for the uptake of MB by KLP.

IV. CONCLUSION AND FINAL REMARKS

The leaves of Kadam tree are an easily available and inexpensive adsorbent. Findings from this investigation revealed that MB adsorption on KLP decreased with increase in initial dye concentration. The optimum amount of adsorbent dosage was found to be 0.4 g/L. The equilibrium contact time was 30 minutes and maximum adsorption took place at pH = 4. Equilibrium data fitted well by Temkin isotherm ($R^2 = 0.94527$) while pseudo second-order kinetic model fitted the kinetics of the adsorption process best. The aforementioned results strongly justify the suitability of KLP as an alternative and low-cost material for the removal of bio-recalcitrant dyes from wastewater.

Declaration of Competing Interest

The authors declare no conflict of interest.

Funding

The authors are highly grateful to the University Grants Commission for providing funds in carrying out this work under the scheme of National Fellowship for Other Backward Classes (NF-OBC).

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Seema Talukdar. "Kinetic study of Methylene blue dye adsorption on *Neolamarckiacadamba* leaves." *IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)*, 16(10), (2022): pp 16-23.