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Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder

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Abstract

The dye, Methylene Blue, was adsorbed on an adsorbent prepared from mature leaves of the Neem tree (*Azadirachta indica*). A batch adsorption study was carried out with variable adsorbate concentration, adsorbent amount, pH, and temperature. Ninety-three percent of the dye could be removed by 2 g of the Neem leaf powder from 1 L of an aqueous solution containing 25 mg of the dye at 300 K. The adsorption followed pseudo first order kinetics with a mean rate constant of 3.73×10^{-3} min^{-1} and an intraparticle diffusion rate constant of 6.36×10^{-2} mg g^{-1} min$^{-0.5}$. A possible mechanism of adsorption was suggested on the basis of concurrently operating surface adsorption and pore diffusion. The experimental data yielded excellent fits with Langmuir and Freundlich isotherm equations. The Langmuir monolayer capacity had a mean value of 8.76 mg g^{-1}. The adsorption of the dye was endothermic in nature (ΔH: 4.62–16.74 kJ mol^{-1}) and was accompanied by an increase in entropy (ΔS: 54.22–90.23 J mol^{-1} K^{-1}) and a decrease in Gibbs energy (ΔG: −10.33 to −13.62 kJ mol^{-1} in the temperature range of 300–330 K). The results indicated that the dye, Methylene Blue, strongly interacts with a biomass-based adsorbent, the Neem leaf powder.

Keywords: Methylene Blue; Dye adsorption; Kinetics; Thermodynamics; Dye removal

1. Introduction

Colour in water is aesthetically unpleasant and may contain appreciable concentration of materials with high oxygen demand and suspended solids. Many dyes and pigments have toxic as well as carcinogenic, mutagenic and teratogenic effects [1] on aquatic life and also on humans [2]. Dyes and pigments are widely used in textile, leather, paper, plastic, and other industries. The effluents of these industries are characterized by fluctuating pH with large load of suspended solids and COD [3]. Some of the dyes and pigments present in these effluents resist biological oxidation and, therefore, they require tertiary treatment [4–6]. Adsorption of dyes and pigments onto granulated activated carbon (GAC) or powdered activated carbon (PAC) is a common practice [7–9]. However, the technology for manufacturing good quality activated carbon is still very cost-prohibitive and the regeneration or disposal of the spent carbon is often problematic. There is also considerable loss of carbon in the waste sludge unless the adsorption is carried out through fixed process. This has prompted the use of various materials as adsorbents in order to develop cheaper alternatives by utilizing agricultural and other wastes. Such low-cost adsorbents have been investigated at the laboratory scale for the treatment of coloured effluents with different degrees of success [3,10–16].

The Neem tree (*Azadirachta indica*) of family Meliaceae is native to the Indian sub-continent, and its seeds and leaves have been used traditionally to treat a number of human ailments and also as a household

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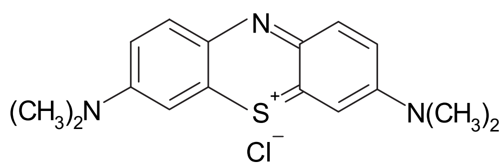
pesticide. The tree itself is known as an air purifier and different parts of the tree such as leaves, bark, and seeds have been reported to possess a variety of medicinal and germicidal properties [17]. Leaves of the tree are used for anti-inflammatory, anxiolytic, anti-androgenic, anti-stress, humoral and cell-mediated immuno-stimulant, anti-hyperglycemic, liver-stimulant, anti-viral, and anti-malarial treatments. In the present work, finely ground Neem leaf powder (NLP) was used as an adsorbent for dyes using aqueous Methylene Blue as a model system. The Neem tree defoliates naturally during January–February each year and the leaves are collect as a waste. The objective of the present work is to utilize the leaves as an adsorbent for dyes and pigments in water and thus, to add a scientific basis to their traditional uses.

Methylene Blue, $C_{16}H_{18}N_3SCl{\cdot}3H_2O$, is a cationic dye having the structure:



The dye is not regarded as acutely toxic, but it can have various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. A large amount creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia-like syndromes.

2. Experimental

2.1. The dye adsorbate and preparation of the adsorbent and the adsorbate

Methylene Blue (Microscopic grade, Glaxo India, Mumbai) was used without further purification. All solutions were made in double distilled water. Mature Neem leaves, collected from a number of Neem trees, were mixed together and washed repeatedly with water to remove dust and other impurities. The leaves were dried first at room temperature in a shade and then in an air oven at 333–343 K for 30 h till the leaves could be crushed into fine powder. The powder was sieved and the 53–74 microfractions were preserved as an adsorbent in glass bottles.

2.2. Adsorption experiments

The adsorption experiments were carried out in a batch process by using aqueous solutions of Methylene Blue. The other variable parameters were adsorbent amount, agitation time and pH of the medium. In each experiment, an accurately weighed amount of NLP was added to 50 mL of the Methylene Blue solution in a 100 mL conical flask and the mixture was agitated in a thermostatic mechanical shaker for a given length of time at a constant temperature. If necessary, the pH was adjusted by addition of a few drops of dilute HNO_3 or NaOH. The mixture was centrifuged (Remi Research Centrifuge) and Methylene Blue remaining unadsorbed ($\lambda_{max} = 663–667$ nm) was determined spectrophotometrically (Hitachi 3210). Calibration curves are obtained with standard Methylene Blue solutions and the amount adsorbed was found by mass-balance procedure.

2.3. Kinetics of adsorption

The kinetics of the adsorption processes was studied by carrying out a separate set of experiments with constant temperature, NLP amount and adsorbate concentration using the pseudo first order Lagergren equation [18]. The differential rate equation is of the form:

$$dq/dt = k_1(q_e - q_t)$$

where q_e and q_t are the amount adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium and at time t, and k_1 is the pseudo first order rate constant (min^{-1}).

Integrating the above equation for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ at $t = 0$, gives:

$$\log(q_e - q_t) = \log q_e - k_1 t/(2.303) \quad (1)$$

A linear plot of $\log(q_e - q_t)$ vs. t verifies the first order kinetics with the slope yielding the value of the rate constant.

2.4. Intra-particle diffusion

The variation in the extent of adsorption with time at different initial dye concentrations was processed for evaluating the role of diffusion in the adsorption system. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion into the interior of the pores. The intra-particle diffusion rate equation [15]:

$$q_t = k_i t^{0.5} \quad (2)$$

where k_i is the intra-particle diffusion rate constant (mg g^{-1} min$^{-0.5}$). The k_i values were calculated from the slopes of the linear plots of q_t vs. $t^{0.5}$.

2.5. Adsorption isotherms

The well-known Freundlich isotherm, Eq. (3), is widely used to describe adsorption on a surface having heterogeneous energy distribution. The Langmuir isotherm, Eq. (4) on the other hand is strictly applicable to monolayer chemisorption. The experimental data are tested with respect to both these isotherms:

$$\text{Freundlich isotherm}: \quad q_e = K_f C_e^n \tag{3}$$

$$\text{Langmuir isotherm}: \quad C_e/q_e = (1/K_d C_1) + (1/C_1) C_e \tag{4}$$

where q_e is the amount of dye adsorbed at equilibrium in unit mass of NLP, C_e is the concentration of the dye in aqueous phase at equilibrium, n and K_f are Freundlich coefficients, C_1 and K_d are Langmuir coefficients. The linear Freundlich and Langmuir plots were obtained by plotting (i) log q_e vs. log C_e and (ii) C_e/q_e vs. C_e, and the adsorption coefficients were computed from the slopes and the intercepts. Another important parameter, R_L, known as the separation factor, could be obtained from the relation:

$$R_L = 1/\left(1 + K_d C_{ref}\right) \tag{5}$$

where C_{ref} is any equilibrium liquid phase concentration of the solute. It has been established [15] that (i) $0 < R_L < 1$ for favourable adsorption, (ii) $R_L > 1$ for unfavourable adsorption, (iii) $R_L = 1$ for linear adsorption, and (iv) $R_L = 0$ for irreversible adsorption.

2.6. Thermodynamic parameters

The Gibbs energy, enthalpy and entropy, (ΔG, ΔH, ΔS), for the adsorption process were obtained from the experiments carried out at different temperatures using the following equations [19]:

$$\log(q_e/C_e) = \Delta S/(2.303R) - \Delta H/(2.303RT) \tag{6}$$

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

where q_e/C_e is called the adsorption affinity, which is the ratio of q_e, the amount adsorbed per unit mass to the solute concentration in unit volume of the solution at equilibrium. The values of ΔH and ΔS were determined from the slope and the intercept of the linear plot of $\log(q_e/C_e)$ vs. $1/T$. These values were used to calculate ΔG.

3. Results and discussion

3.1. Kinetics of adsorption

The kinetics of Methylene Blue adsorption on NLP was studied with respect to different amounts of the adsorbent (Fig. 1). The extent of adsorption varied in a narrow range from 85.0% (NLP 2 g/L, agitation time 1 h) to 95.0% (NLP 10 g/L, agitation time 5 h). The interactions appeared to attain equilibrium rapidly after about 1 h of agitation.

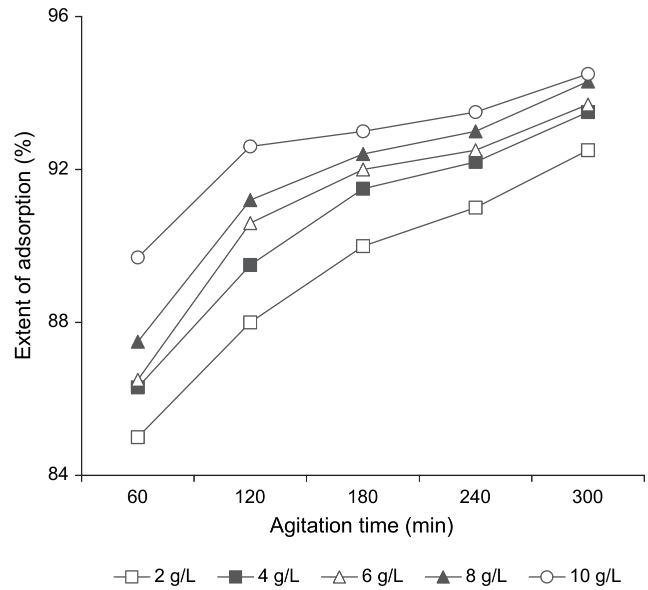


Fig. 1. Extent of adsorption (%) of the dye Methylene Blue on different amounts of the adsorbent, Neem leaf powder at 300 K (dye concentration 40 mg/L).

Assuming pseudo first order kinetics for the adsorption process, $\log(q_e - q_t)$ was plotted against t and the linearity of the Lagergren plots (Fig. 2) confirmed the same (the correlation coefficients for the plots were in the range 0.92–0.99). The first order rate constants evaluated from these plots were between 2.99×10^{-3} and $5.07 \times 10^{-3}\ \text{min}^{-1}$ for different amounts of the adsorbent (mean value $3.73 \times 10^{-3}\ \text{min}^{-1}$). The

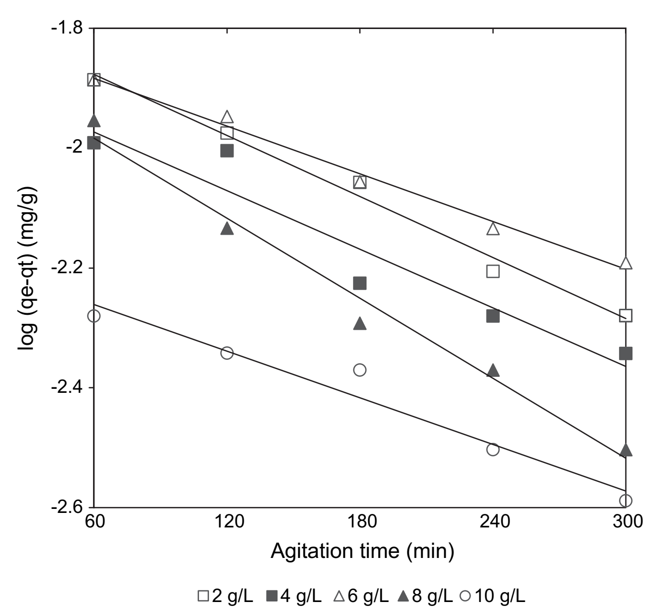


Fig. 2. Lagergren plots for adsorption of Methylene Blue on Neem leaf powder at 300 K (dye concentration 50 mg/L).

dye–NLP interactions could thus be predicted as reasonably fast. It may be noted that the pseudo first order reaction differs from a true first order reaction in two aspects: the expression $k_1(q_e-q_t)$ does not represent the number of available sites and the parameter log q_e is an adjustable parameter whose value is not equal to the intercept of the plot of $\log(q_e-q_t)$ vs. t [15]. In the present work, the intercepts of the Lagergren plots were very close to the theoretical log q_e values, and therefore, the kinetics of Methylene Blue adsorption on Neem leaf powder could be considered as almost true first order in nature. Further, the difficulty usually associated with the application of the pseudo first order model to an adsorption system arising from the uncertainty of finding reliable q_e values within a reasonable time was not applicable in the present work as the system was very close to equilibrium even after 1 h of agitation time.

A number of authors have reported pseudo first order kinetics for adsorption of dyes on various adsorbents prepared from biological sources similar to the Neem leaf powder. The values of the rate constant, k_1, obtained by these workers are compared with the values obtained in the present work in Table 1 (conditions vary). It is to be noted that the first order rate constant for the interaction of Methylene Blue with Neem leaf powder, k_1, in the present work were 10–100 times less when compared to the values obtained for adsorption of Methylene Blue on water hyacinth roots (4.2×10^{-2}–6.9×10^{-2} min^{-1}) [20], on banana peel (3.5×10^{-1} min^{-1}) and orange peel (2.9×10^{-1} min^{-1}) [21].

3.2. Intra-particle diffusion

The plots of q_t vs. $t^{0.5}$ (Fig. 3) were found to be linear with regression coefficients of 0.90–0.99. The

Table 1
Pseudo first order rate constant data for adsorption of dyes on various adsorbents

Adsorbent	Dyes	k (min^{-1})	Reference
Banana pith	Acid Violet	$(1.8–13.0) \times 10^{-2}$	[33]
Orange peel	Rhodamine B	$(2.3–9.95) \times 10^{-1}$	[13]
Water hyacinth	Methylene Blue	$(4.2–6.9) \times 10^{-2}$	[20]
Orange peel	Congo Red	$(3.6–4.9) \times 10^{-2}$	[13]
	Procion Orange	$(8.3–15.5) \times 10^{-2}$	[13]
	Rhodamine-B	$(9.9–29.9) \times 10^{-2}$	[13]
Pith	Basic Red 22	$(1.0–1.1) \times 10^{-2}$	[34]
	Acid Red 114	$(8.9–9.5) \times 10^{-3}$	[4]
Orange peel	Acid Violet 17	$(3.5–6.9) \times 10^{-2}$	[3]
Banana peel	Methyl Orange	3.9×10^{-1}	[21]
	Methylene Blue	3.5×10^{-1}	[21]
	Rhodamine B	1.9×10^{-1}	[21]
Orange peel	Methyl Orange	4.0×10^{-1}	[21]
	Methylene Blue	2.9×10^{-1}	[21]
	Rhodamine B	2.1×10^{-1}	[21]
Coir pith	Congo Red	$(2.1–3.9) \times 10^{-1}$	[32]
Neem leaf powder	Brilliant Green	7.32×10^{-3}	[28]
Neem leaf powder	Methylene Blue	$(2.9–5.1) \times 10^{-3}$	This work

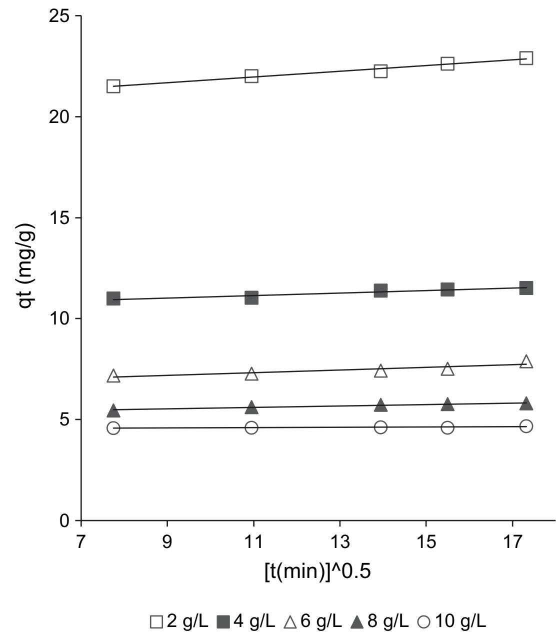


Fig. 3. Plots of q_t (mg g^{-1}) vs. $t^{0.5}$ for evaluating intra-particle diffusion rate constant (Methylene Blue concentration 40 mg/L, temperature 300 K).

intra-particle diffusion rate constant, k_i, was in the range of $(1.21–14.17) \times 10^{-2}$ mg g^{-1} min$^{-0.5}$ (mean $k_i = 6.36 \times 10^{-2}$ mg g^{-1} min$^{-0.5}$). The linearity of the plots demonstrated that intra-particle diffusion played a significant role [21] in the uptake of the dye by Neem leaf powder. This also confirms that adsorption of the dye on the adsorbent was a multi-step process, involving adsorption on the external surface and diffusion into the interior. All the steps slow down as the system approaches equilibrium. If the steps are independent of one another, the plot of q_t vs. $t^{0.5}$ usually shows two or more intersecting lines depending on the exact mechanism, the first one of these lines representing surface adsorption and the second one intra-particle diffusion. The absence of such features in the plots of the present work indicated that the steps were indistinguishable from one another and that the intra-particle diffusion was a prominent process right from the beginning of dye–solid interaction. The cationic dye molecules thus easily penetrated the pore structure in the particles of the Neem leaf powder. Still it would not give sufficient indication about which of the two steps was the rate-limiting step. Weber and Morris [22] have proposed that if the uptake of the adsorbate varies with the square root of time, intra-particle diffusion can be taken as the rate-limiting step. Ho [23] has shown that it is essential for the q_t vs. $t^{0.5}$ plots to go through the origin if the intra-particle diffusion is the sole rate-limiting step. Since this was also not the case in the present work (the q_t vs. $t^{0.5}$ plots have intercepts in the range 4.50–20.40 mg g^{-1}), it may be concluded that surface adsorption and intra-particle diffusion were concurrently operating during the Methylene Blue–NLP interactions.

3.3. Effect of the amount of adsorbent and the initial concentration of the adsorbate

To investigate the effect of adsorbent mass on amount of adsorption, a series of experiments were carried out keeping the agitation time constant and varying both the amount of adsorbent and the adsorbate concentration at constant temperature. For a Neem leaf powder of 2 g/L, the amount adsorbed increased from 11.63 to 30.66 mg g^{-1} as the Methylene Blue concentration was increased from 25 to 70 mg/L (Table 2). On the other hand, for a constant dye concentration of 25 mg/L, the amount adsorbed decreased from 11.63 to 2.38 mg g^{-1} as the adsorbent mass was changed from 2 to 10 g/L. The results as a whole indicate two distinct trends: the amount adsorbed, q_t (mg g^{-1}), increased with an increase in the dye concentration and decreased with an increase in the amount of the adsorbent. The latter trend may be due to the effect of adsorbent mass on porosity of the adsorbent suspension. In general, the trends might have been influenced by changes in a number of physical properties of the solid–liquid suspensions including their viscosity.

3.4. Effect of pH

The pH of the medium did not show any significant effect on uptake of Methylene Blue by NLP. With pH of the medium varying from 2.0 to 10.0, the adsorption of the dye oscillated between 97.3 and 97.8%. Ho et al. [24] have shown that the extent of removal of a basic dye (Basic Red 18) by activated clay decreased rapidly as pH increased from 3.0 to 5.0 and from 8.0 to 10.0. However, the adsorption remained constant within the range of pH 5.0–8.0. It was suggested that the increase in sorption depended on the properties of the adsorbent surface and the dye structure. At a lower pH, the adsorbent surface might have become negatively charged attracting more of the basic dye molecules. It is likely that positive charge develops on the surface of an adsorbent in an acidic medium, resulting in a higher adsorption of anionic dyes than in a basic solution. If this is the case, the sorption of the cationic dye should decrease at a lower pH. In addition, the effect of pH may also be explained on the basis of surface hydroxylation, acid–base dissociation and surface complex formation. The insignificant pH-dependence of the results obtained in the present work, as distinct from the above, was more likely to be due to the differences in the properties of the adsorption sites of the Neem leaf powder.

Summers and Roberts [25] have reported for the granulated activated carbon (GAC) adsorbent that the chemical nature of the surface is influenced by solution pH, which therefore plays an important role in the adsorption of solutes from aqueous solutions. At a lower pH, the molecular form is the predominantly adsorbed species, while at a higher pH, the ionized form is preferentially adsorbed. The results in the present study may be interpreted if the NLP surface had equal preference for molecularly adsorbed Methylene Blue species and dissociated cationic species.

The active ingredients in the Neem leaves have been identified as "triterpenes", or more specifically "limonoids", belonging to a general class of natural products and the dominant ones present in Neem are *azadirachtin*, *salannin*, *meliantriol*, *nimbin* and *nimbidin* [26,27]. These natural products contain a number of phenolic-OH groups as well as COO^- groups. Therefore, the effect of pH on the solid–liquid equilibrium can be explained on the basis of three possible mechanisms: (i) chemical interaction between OH groups of active components of Neem leaves and the reactive group (Cl^-) of Methylene Blue (with elimination of HCl), (ii) chemical interaction between COO^- groups of the active components of Neem and the dye cations and (iii) weak electrostatic interaction between the cationic dye and electron-rich sites of the surface of the NLP particles. The pH of the medium would definitely influence the course of the first two mechanisms, but the third mechanism may operate over a large range of pH without being affected much. The amount adsorbed in the present work remained nearly constant in the pH-range of 2.0–10.0, and therefore, the adsorption of

Table 2
Amount of Methylene Blue (MB) adsorbed on Neem leaf powder at 300 K in mg g^{-1}

MB (mg/L)	Amount adsorbed (mg g^{-1}) for NLP amount of				
	2 g/L	4 g/L	6 g/L	8 g/L	10 g/L
25	11.63 (93.0)	5.94 (94.0)	3.96 (94.8)	2.97 (95.0)	2.38 (95.2)
30	13.88 (92.5)	7.05 (93.6)	4.68 (94.0)	3.53 (94.2)	2.84 (94.5)
40	18.2 (91.0)	9.32 (92.0)	6.13 (93.2)	4.65 (93.0)	3.74 (93.5)
50	22.63 (90.5)	11.44 (90.0)	7.50 (91.5)	5.76 (92.0)	4.60 (92.2)
60	26.70 (89.0)	13.58 (89.0)	8.90 (90.5)	6.86 (91.5)	5.52 (92.0)
70	30.66 (87.6)	15.58 (88.0)	10.27 (89.0)	7.88 (90.0)	6.41 (91.5)

Contact time 4 h; data inside parentheses give percentage adsorbed.

Methylene Blue on NLP might be attributed to weak electrostatic interactions between the dye molecules and the solid surface.

3.5. Adsorption isotherms

The experimental data yielded good linear plots with both Freundlich isotherm (Fig. 4, Regression coefficient $R \approx 0.99$) and Langmuir isotherm (Fig. 5, R: 0.96–0.99). The adsorption coefficients computed from the plots are given in Table 3. The Freundlich coefficient, n, which should have values in the range of $0 < n < 1$ for favourable adsorption, remained in a narrow range of 0.51–0.66 for different amounts of the adsorbent. The Freundlich adsorption capacity, K_f, was in the range of 2.42–9.47 L g^{-1}.

The Langmuir monolayer adsorption capacity, C_1, was large with values between 3.67 and 19.61 mg g^{-1}. The Langmuir adsorption intensity, K_d, had values of 0.186–0.729 L mg^{-1}. The dimensionless separation factor, R_L, had an average value of 0.96 in the range of 0.91–0.98 in concurrence with the suggested values for favourable adsorption. This value being very close to 1.0, the adsorption of the dye on NLP could be described as linear in nature, i.e., there was an almost linear increase in adsorption with increase in NLP amount. The isotherm constants indicated that the Neem leaf powder had very good potential as an adsorbent for the dye, Methylene Blue, and it might have similar potential for other dyes, as had already been demonstrated for Brilliant Green [28].

The Langmuir monolayer capacity of the Neem leaf powder (3.67–19.61 g kg^{-1}, mean value 8.76 g kg^{-1}) may be compared with a number of adsorbents derived from biological sources like the Neem leaf powder (Table 4). Some of the large adsorption capacities recorded were: 160 g kg^{-1} for Atrazon Blue on Maize cob [29], 94.5 g kg^{-1} for Maxilon Red also on Maize cob [29], and 133.7 g kg^{-1} for Brilliant Green on Neem leaf powder [28].

It is significant that the Freundlich plots are nearly parallel to one another with very similar slopes, but the Langmuir plots have converged towards the origin with appreciable differences in slopes. This might be due to lack of uniformity in size, shape and surface energy of the NLP particles – the combined effect of which is

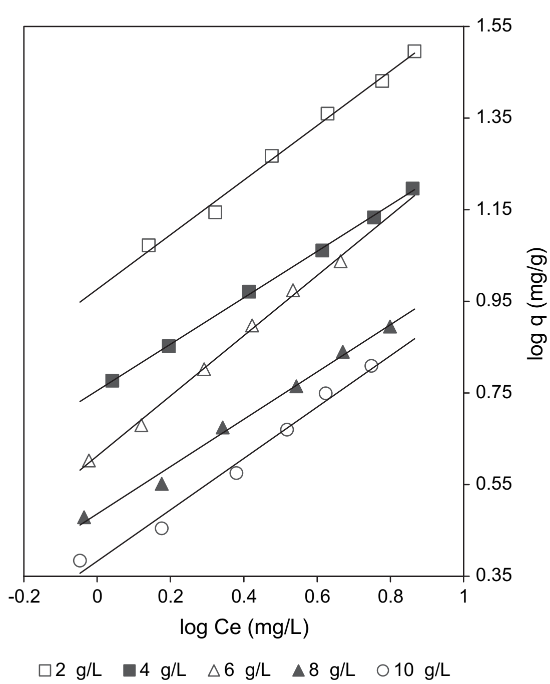


Fig. 4. Freundlich isotherms for adsorption of Methylene Blue on Neem leaf powder at 300 K with dye concentration of 50 mg/L and agitation time 5 h.

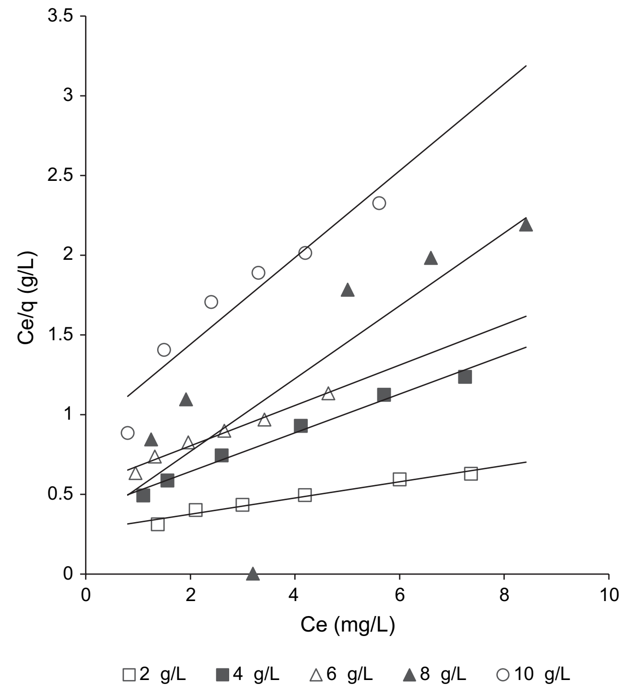


Fig. 5. Langmuir isotherms for adsorption of Methylene Blue on Neem leaf powder at 300 K with dye concentration of 50 mg/L and agitation time 5 h.

Table 3
Freundlich and Langmuir adsorption coefficients for adsorption of Methylene Blue on Neem leaf powder at 300 K.

Adsorbent (g/L)	Freundlich constants		Langmuir constants		
	n	K_f (L g^{-1})	K_d (L g^{-1})	C_1 (mg g^{-1})	R_L
2	0.60	9.47	186.3	19.61	0.98
4	0.51	5.67	303.8	8.23	0.96
6	0.66	4.09	229.9	7.89	0.97
8	0.52	3.06	728.5	4.41	0.91
10	0.56	2.42	304.0	3.67	0.96
Mean	0.57	4.95	351.0	8.76	0.96

Contact time 5 h, dye concentration 50 mg/L.

Table 4
Comparison of the monolayer adsorption capacities of some dyes on various adsorbents

Dyes	Adsorbents	C_1 (g kg^{-1})	Reference
Telon Blue	Maize cob	41.4	[29]
Atrazon Blue	Maize cob	160.0	[29]
Maxilon Red	Maize cob	94.5	[29]
Erionyl Red	Maize cob	47.7	[29]
Acid Violet 17	Orange peel	19.88	[3]
Congo Red	Coir pith	6.72	[32]
Methyl Orange	Banana, Orange peel	21.0, 20.5	[21]
Methylene Blue	Banana, Orange peel	20.8, 18.6	[21]
Rhodamine B	Banana, Orange peel	20.6, 14.3	[21]
Congo Red	Banana, Orange peel	18.2, 14.0	[21]
Methyl Violet	Banana, Orange peel	12.2, 11.5	[21]
Amino Black	Banana, Orange peel	6.5, 7.9	[21]
Brilliant Green	Neem leaf powder	133.69	[28]
Methylene Blue	Neem leaf powder	3.67–19.61	This work

likely to be accentuated with increasing NLP amount. The large dye molecules would occupy an appreciable amount of area on the surface of the NLP particles and even if the number of dye molecules adsorbed on the surface might not be large, the high molecular mass would ensure a substantial monolayer capacity. Further, the Langmuir coefficient, K_d, related to the equilibrium constant of the adsorption process, has sufficiently large values (range: 186.3–728.5 L g^{-1}, mean value 351.0 L g^{-1}) indicating that the equilibrium

NLP + Methylene blue = [NLP–dye complex]

is shifted predominantly to the right leading to uptake of dye molecules by the NLP surface. The Neem leaf powder thus has good potential to be used as an adsorbent for the removal of Methylene Blue from water.

3.6. Effect of temperature and thermodynamic parameters

When the adsorption was carried out at five different temperatures from 300 to 340 K with an interval of 10 K, the extent of adsorption improved steadily with an increase in adsorption temperature, and the most pronounced change occurring between 300 and 310 K (Fig. 6). The Methylene Blue adsorption on the Neem leaf powder was definitely endothermic in nature requiring some amount of activation.

The thermodynamic parameters for the adsorption process (Table 5) were computed from the log(q_e/C_e) vs. $1/T$ plots (Fig. 7) for a constant NLP amount of 2 g/L with an agitation time of 5 h. These plots have very good linearity with regression coefficient varying from 0.93 to 0.99. The ΔH values were in the range of 4.62–16.74 kJ mol^{-1} with a mean value of 9.40 kJ mol^{-1}. The values conform to the endothermic nature of the adsorption process. Similar endothermic adsorption of Methylene Blue was observed earlier on Guyava leaves

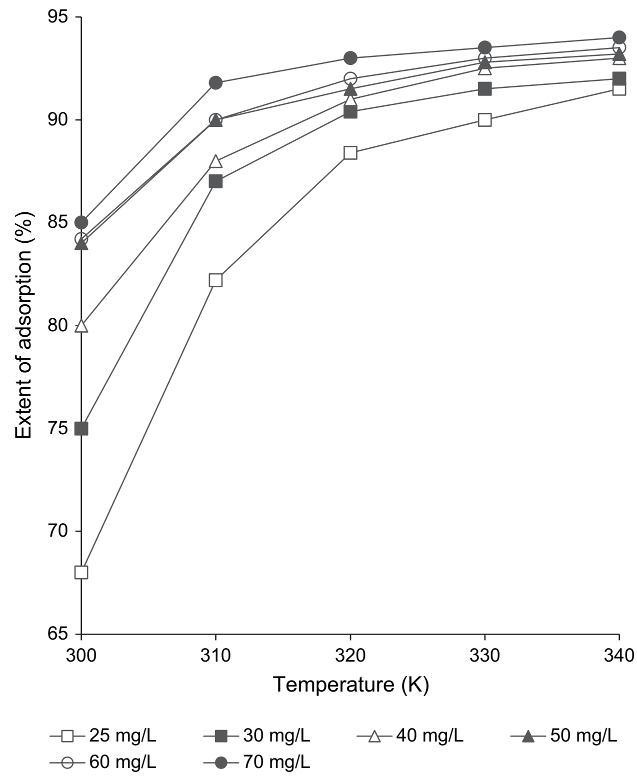


Fig. 6. Effect of temperature on extent of adsorption (%) of Methylene Blue on NLP (agitation time 5 h, NLP amount 2 g/L).

[30] and kaolinite [31]. The small values of ΔH were not compatible with the formation of strong chemical bonds between the dye molecules and the NLP, and the adsorption process was likely to be due to weak electrostatic interactions as discussed already.

The adsorption process resulted in an increase in entropy of the system from 54.22 to 90.23 J mol^{-1} K^{-1} (mean value 68.84 J mol^{-1} K^{-1}). Usually adsorption of gases on solids is accompanied by a decrease in entropy as the molecules from the disordered gaseous state find an ordered arrangement on the surface of the solids. In case of adsorption from solutions, it was likely that the dye molecules on the NLP surface were more chaotically arranged compared to the situation in the aqueous solution. The large Methylene Blue molecules might be

Table 5
Thermodynamic parameters for adsorption of Methylene Blue on Neem leaf powder (2 g/L) after an agitation time of 5 h

Dye (mg/L)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	$-\Delta G$ (kJ mol^{-1}) at temperatures			
			300 K	310 K	320 K	330 K
25	16.74	90.23	10.33	11.24	12.14	13.04
30	7.87	63.36	11.14	11.77	12.41	13.04
40	9.06	68.05	11.36	12.04	12.72	13.40
50	9.94	71.38	11.48	12.19	12.90	13.62
60	8.17	65.77	11.56	12.22	12.88	13.54
70	4.62	54.22	11.65	12.19	12.74	13.28
Mean	9.40	68.84	11.26	11.94	12.63	13.32

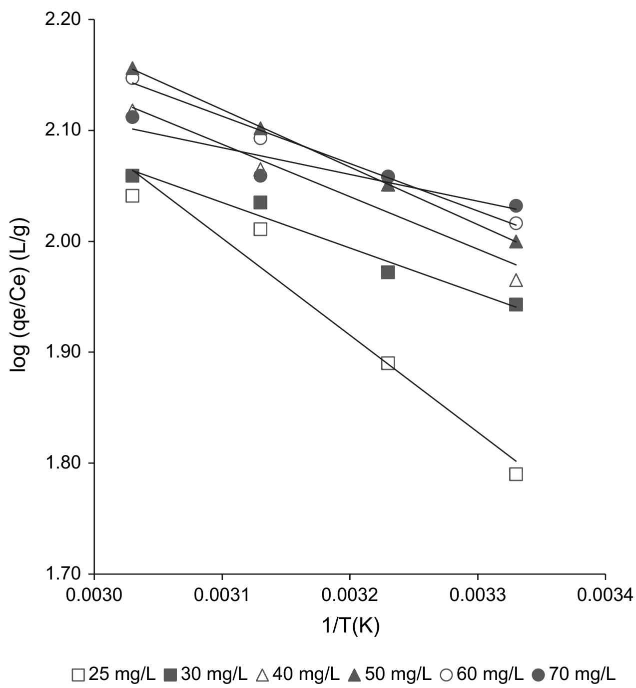


Fig. 7. The plots of $\log(q_e/C_e)$ vs. $1/T$ for adsorption of Methylene Blue at temperatures of 300, 310, 320, and 330 K (agitation time 5 h, NLP amount 2 g/L).

responsible for this. The positive values of ΔS confirm a high preference of Methylene Blue molecules for the NLP surface and suggest possibility of some structural changes or readjustments in the Methylene Blue–NLP adsorption complex [23].

Despite being endothermic in nature, the spontaneity of the adsorption process was ensured by a decrease in the Gibbs energy of the system. The ΔG values varied in a narrow range with the mean values showing a gradual increase from -11.26 to -13.32 kJ mol^{-1} in the temperature range of 300–330 K in accordance with the endothermic nature of the adsorption process. The parameters, ΔH, ΔS, and ΔG, for the Methylene Blue–NLP interactions changed in a way that made the adsorption thermodynamically feasible with a high degree of affinity of the dye molecules for the NLP surface.

Ghosh and Bhattacharyya [31] have reported ΔH, ΔS and ΔG values in the ranges of 6.03–13.53 kJ mol^{-1}, 69.69–88.16 J mol^{-1} K^{-1}, and -13.85 to -15.61 kJ mol^{-1}, respectively, for endothermic adsorption of Methylene Blue on six kaolinite-based adsorbents. Endothermic uptake of the neutral dye, Congo Red on activated carbon made from coir pith was observed by Namasivayam and Kavitha [32] with ΔH value of 7.71 kJ mol^{-1}. The adsorption of the basic dye, Brilliant Green on Neem leaf powder was also found to be endothermic in nature with mean ΔH, ΔS, ΔG values of 12.12 kJ mol^{-1}, 67.02 J mol^{-1} K^{-1}, and -8.64 kJ mol^{-1}, respectively [28]. These values are very much comparable to the ones obtained in the present work.

4. Conclusion

The results of this work can be summarized as follows:

(i) Neem leaf powder is a promising adsorbent for removal of the cationic dye, Methylene Blue from water. A small amount (2 g/L) of the adsorbent could almost completely decolorize an aqueous solution of Methylene Blue (40 mg/L) if agitated for 5 h.

(ii) The solution pH did not have important bearing on the extent of adsorption of the dye on NLP, ruling out charging of the NLP surface in a particular pattern (either positively or negatively) and indicating that the nature of the surface sites rather than the pH of the medium controlled the adsorption process.

(iii) The experimental data produced perfect fit with the Freundlich isotherm showing that the surface of the NLP particles was heterogeneous, non-specific and non-uniform in nature. The mechanism of the dye–NLP interactions is thus likely to be very complicated involving a wide range of sites differing in a number of aspects including energy considerations.

(iv) The data were in good agreement with the Langmuir isotherm. However, the interactions did not appear to be driven purely by chemical forces as subsequently found from the thermodynamic data.

(v) The adsorption of the dye on NLP followed pseudo first order kinetics with the interactions largely over within the first hour.

(vi) The adsorption of Methylene Blue on NLP was slightly endothermic indicating that a temperature above the ambient temperature would be favourable for carrying out the removal of the dye. However, adsorption is quite high even at ambient temperature.

The Neem tree regularly sheds its leaves during January–February, which become waste. These leaves can be put to good use as an adsorbent for removal of colour from industrial and other effluents. However, as with all other bio-resources, the processes are likely to be very complicated and a detailed characterization of the surface will be necessary to develop more insight into the mode of action.

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