Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Dyes and Pigments 57 (2003) 211–222
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Adsorption characteristics of the dye, Brilliant Green, on Neem leaf powder

Krishna G. Bhattacharyya*, Arunima Sarma

Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India

Received 4 October 2002; received in revised form 15 November 2002; accepted 6 January 2003

Abstract

A novel adsorbent was developed from mature leaves of natural Neem trees for removing dyes from water. The adsorbent, in the form of fine powder, was found to be very effective in removing the dye, Brilliant Green, from aqueous solution. The adsorption process was carried out in a batch process with different concentrations of the aqueous dye solution as well as with different adsorbent doses, at a range of pH values and temperature. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir and Freundlich isotherms and by computing equilibrium thermodynamic and kinetic parameters, the values of which showed the Neem leaf powder as a promising adsorbent for dyes in aqueous solution.

Keywords: Neem leaf powder; Brilliant Green; Colour removal; Adsorption

1. Introduction

The Neem tree (*Azadirachta indica*) of family *meliaceae* is native to the Indian sub-continent, and its seeds and leaves have been in use since ancient times to treat a number of human ailments and also as a household pesticide [1–4]. The tree itself is known as an air purifier and a variety of medicinal and germicidal properties have been attributed to leaves, bark, seeds and other parts of the plant [5]. Leaves of the tree are used as anti-inflammatory, anxiolytic, anti-androgenic, anti-stress, humoral and cell-mediated immunostimulant, anti-hyperglycemic, liver-stimulant, anti-viral and anti-malarial activities [6].

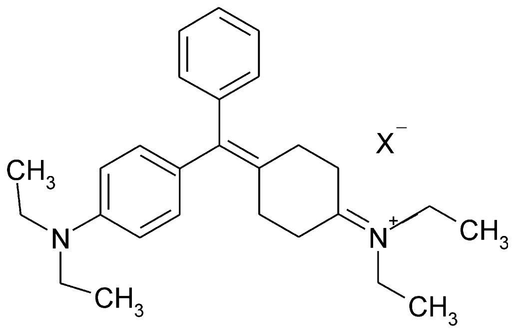
Many industries generate coloured effluents containing various dyes and pigments and discharge the same to natural water bodies. Such effluents are characterized by fluctuating pH with large load of suspended solids and high oxygen demand [7]. The textile industry and the pulp and paper mills discharge highly colored effluents, which retain their colour even after going through the conventional biological treatment process unless tertiary treatment measures [8–10] are taken to remove colour by adsorption on activated carbon, etc. Many dyes and pigments are toxic and have carcinogenic and mutagenic effects [11–12] that affect aquatic biota and also humans [13].

* Corresponding author. Tel.: +91-361-571529; fax: +91-361-570133.
E-mail address: krishna111@sancharnet.in (K.G. Bhattacharyya).

0143-7208/03/$ - see front matter
doi:10.1016/S0143-7208(03)00009-3

Industries use biological treatment, coagulation, floatation, oxidation, hyper filtration and adsorption for removing colour from the aqueous medium. Biological treatment is not found to be advantageous as it requires large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Adsorption onto granulated activated carbon (GAC) or powdered activated carbon (PAC) is widely practiced [14–16], particularly for the removal of the persistent organics. However, adsorbent-grade activated carbon is cost-prohibitive and regeneration of the used carbon is not straightforward. Many novel materials have been tested as adsorbents with a two-fold objective—to replace activated carbon with cheaper alternatives and to utilize various waste products for the purpose. Such low cost adsorbents have found use at least in laboratory scale for treatment of coloured effluents with different degrees of success [17–23]. In a recent work, crushed fruit wastes such as banana and orange peels [24] have been used to remove a number of dyes from aqueous solution, while carbons made from coir pith wastes [25] have been tried as adsorbents to remove Congo Red from water.

In the present work, finely ground Neem leaf powder (NLP) has been used as an alternative to activated carbon for removing the dye, Brilliant Green from aqueous medium. The dye, which has the molecular formula, $C_{27}H_{34}N_2O_4S$, has the following structure:



The dye causes eye burns, which may be responsible for permanent injury to the eyes of humans and animals. If swallowed, the dye causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also be harmful if inhaled. It is likely to cause irritation to the skin and the respiratory tract. Symptoms may include coughing and shortness of breath. On decomposition, it may form harmful carbon oxides, nitrogen oxides, and sulfur oxides. It is therefore essential to remove this dye from water.

2. Experimental

Mature Neem leaves, collected from a number of tall Neem trees (District Morigaon, Assam, India) were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry first at room temperature in a shade and then in an air oven at 333–343 K for a long time till the leaves became crisp that could be crushed into a fine powder in a mechanical grinder. The NLP was sieved and the 200–300 mesh fraction was separated. This fraction was again washed a number of times with double distilled water till the washings are free of colour and turbidity. After drying for several hours at room temperature, the NLP was preserved in glass bottles for use as an adsorbent.

The dye, Brilliant Green (Qualigens, Mumbai) was used without further purification. A stock solution containing 100 mg of the dye in 1 dm^3 was made by dissolving the required amount of the dye in double distilled water. For concentration determination by spectrophotometric method, a number of standard solutions were made from the stock solution in the concentration range 10–50 mg dm^{-3} for reading absorbance at $\lambda_{max} = 624$ nm from which the calibration curve was drawn.

The pH of the aqueous solutions of Brilliant Green was ~6.5 which did not change much with dilution. The dye solution is pH-sensitive, it becomes turbid if the pH is lowered and it changes colour if the pH is increased. Therefore, all the adsorption experiments were done without adjusting the pH. The batch adsorption was carried out in 100 ml borosil conical flasks by mixing a pre-weighed amount of the NLP with 50 ml of the aqueous dye solution of particular concentration. The conical flasks were kept in a constant temperature, water bath shaker (NSW) and were shaken for a pre-determined time interval at a fixed speed. The adsorbent dose, contact time and temperature of adsorption were carefully controlled. After adsorption was over, the mixture was rapidly centrifuged in a laboratory centrifuge. The adsorbent settled quickly and the dye remaining unadsorbed was determined spectrophotometrically (Perkin-Elmer Lambda EZ-201).

The most widely used two-parameter equation, describing the adsorption process is the Langmuir equation, which has the form:

$$\theta = q_e/C_1 = K_d C_e/(1 + K_d C_e) \quad (1)$$

where θ is the fractional coverage and C_1 is the amount adsorbed per unit mass of the adsorbent corresponding to formation of a complete monolayer, K_d is the Langmuir constant related to the equilibrium constant of the adsorption equilibrium. C_e and q_e are the equilibrium liquid phase concentration and amount of solute adsorbed at equilibrium, respectively. Eq. (1) can be rearranged to the form:

$$C_e/q_e = (1/K_d \ C_1) + (1/C_1)C_e \quad (2)$$

which shows that a plot of (C_e/q_e) vs. C_e should give a straight line if the Langmuir equation is obeyed by the adsorption equilibrium and the slope and the intercept of this line will give the values of C_1 and K_d. These expressions have been shown to be valid in higher concentration ranges [26]. For lower concentrations, the following form of Langmuir equation is found to be more satisfactory [27]:

$$1/q_e = (1/C_1) + (1/K_d C_1)(1/C_e) \quad (3)$$

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [26], also known as the separation factor given by

$$R_L = 1/(1 + K_d C_{ref}) \quad (4)$$

where C_{ref} is any equilibrium liquid phase concentration of the solute. It is shown that for favourable adsorption, $0 < R_L < 1$, while $R_L > 1$ represents unfavourable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$ [28].

Another empirical isotherm given by the Freundlich equation is often used to describe the adsorption data. This equation has the form

$$q_e = K_f C_e^n \quad (5)$$

where K_f and n are known as Freundlich coefficients which can be determined from the plots of $\log q_e$ versus $\log C_e$ on the basis of the linear form of the equation

$$\log \ q_e = \log \ K_f + n \ \log \ C_e \quad (6)$$

The thermodynamic parameters for the adsorption process, namely Gibbs energy (ΔG^0), enthalpy of adsorption (ΔH^0), and entropy of adsorption (ΔS^0) are determined by carrying out the adsorption experiments at four different temperatures and using the following equations [29]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

$$\log \ (q/C_e) = -\Delta H^0/(2.303RT) + \Delta S^0/(2.303R) \quad (8)$$

where (q/C_e) is called the adsorption affinity and is the ratio of q, the amount adsorbed per unit mass (mmol/g) to C_e, the equilibrium concentration (mmol dm^{-3}) of the solute. The values of ΔH^0 and ΔS^0 were determined from the slope and the intercept of the linear plot of log (q/C_e) versus $1/T$. These values were used to calculate ΔG^0.

The kinetics of the adsorption processes was studied by carrying out a separate batch of experiments at constant temperature with a fixed NLP dose and a fixed adsorptive concentration and by using the simple Lagergren equation [30,31]:

$$\log \ (q_e - q) = \log \ q_e - k_{ad}.t/(2.303) \quad (9)$$

where q_e and q are the amounts adsorbed (mmol/g) at equilibrium and at any time t, k_{ad} is the adsorption rate constant in s^{-1}. Plot of log $(q_e - q)$ vs. t gives a straight line for first order adsorption kinetics, which allow computation of the adsorption rate constant, k_{ad}. The variation in the amount of adsorption with time at different initial dye concentrations was further processed for evaluating the role of diffusion in the adsorption of the dye on to NLP powder. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates and, then, diffusion of the solute molecules into the interior of the pores—which is likely to be a slow process and is therefore, rate determining [32]. The rate, q_t, for intra-particle diffusion (k_p) is given by Eq. [33]:

$$q_t = k_p.t^{1/2} \quad (10)$$

where k_p is the intra-particle diffusion rate constant.

3. Results and discussion

The percentage adsorption of the dye, Brilliant Green, on NLP steadily increased with an increase in the contact time. This is more pronounced for the lower doses of NLP. For example, a NLP dose of 0.13 g dm^{-3} showed 25% adsorption at 1-h contact time, but the adsorption increased to 71.8% after 5 h. On the other hand, if the NLP dose was increased to 0.63 g dm^{-3}, the adsorption percentage only changed from 90% at 1 h to 98% at 5 h. The variations in percent adsorption are shown in Fig. 1 for a fixed dye concentration at 300 K. The results show that by choosing an appropriate dose of NLP, it will be possible to remove the dye, Brilliant Green, almost completely from aqueous medium. The data for the amount of the dye adsorbed per unit mass of NLP (in mmol g^{-1}) for a fixed dose of the adsorbent with different concentrations of the dye solution are presented in Table 1(a), which indicate only small differences with increase in contact time. Thus, if the adsorbent dose and adsorptive concentration are kept constant, unit mass of the adsorbent has an almost constant uptake of the dye independent of the concentration of the dye solution. If, however, the amount adsorbed is expressed in mg g^{-1}, considerable increase with contact time was observed at lower NLP doses for a fixed dye concentration [Table 1(b)]. For a small dose of NLP, diffusion into the pores may be the rate-determining step, which is likely to be very slow, and therefore, a large contact time is required to yield better results.

The Lagergren plots (Fig. 2) of log (q_e−q) vs. t yield near-perfect straight lines that show the adsorption of the dye Brilliant Green on NLP to follow first order kinetics. Thus, after an initial fast rate of adsorption of the dye on NLP, the kinetics become slow and the removal of the dye

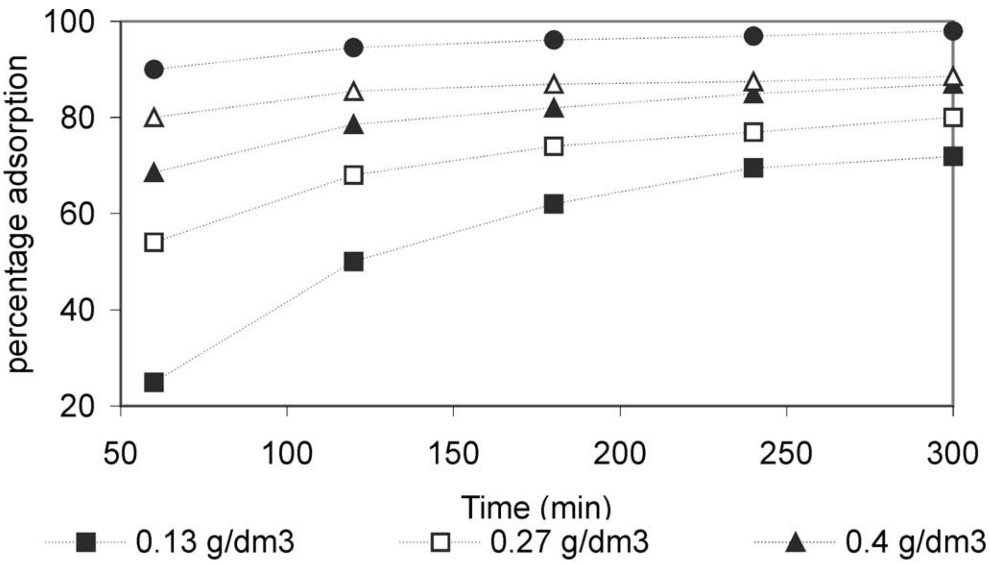


Fig. 1. Variation of adsorption (in percentage) of the dye, Brilliant Green, with contact time for different NLP doses at 300 K (dye concentration: 8.29 × 10^{-2} mmol/dm^{-3}).

from the aqueous solution will follow an exponential pattern. The first order rate constant of adsorption has the mean value of 7.32×10^{-3} min^{-1}, which may be considered as reasonable for practical applications. The intra-particle diffusion rate, obtained from the plots of q_t (amount adsorbed in mmol per unit mass (g) of the adsorbent after a contact time of t min) vs. $t^{1/2}$ (Fig. 3) has the mean value of 8.12×10^{-4} mmol g^{-1} $min^{-1/2}$. This shows that the intra-particle diffusion is much

Table 1
Dependence of Brilliant Green adsorption on contact time with Neem leaf powder at 300 K for (a) a NLP dose of 0.63 g dm^{-3}, (b) for dye concentration of 8.29×10^{-2} mmol dm^{-3}

Time (min)	q (mmol g^{-1}) $\times 10^2$, i.e. amount of dye adsorbed per unit mass of NLP for dye concentration (mmol dm^{-3}) of				
	2.07×10^{-2}	4.14×10^{-2}	6.23×10^{-2}	8.29×10^{-2}	10.36×10^{-2}
(a)					
60	3.08	6.14	9.18	11.19	11.50
120	3.08	6.14	9.18	11.75	13.52
180	3.08	6.15	9.19	11.96	13.83
240	3.09	6.17	9.21	12.06	13.99
300	3.10	6.19	9.25	12.18	14.61
	q (mg/g), i.e. amount of dye adsorbed per unit mass of NLP at dose				
	0.13 g dm^{-3}	0.27 g dm^{-3}	0.4 g dm^{-3}	0.53 g dm^{-3}	0.63 g dm^{-3}
(b)					
60	103.0	81.5	68.5	63.0	54.0
120	150.0	92.5	78.5	64.1	56.7
180	186.0	105.0	82.0	65.3	57.7
240	208.5	111.0	85.0	65.6	58.2
300	215.5	112.5	87.0	66.4	58.8

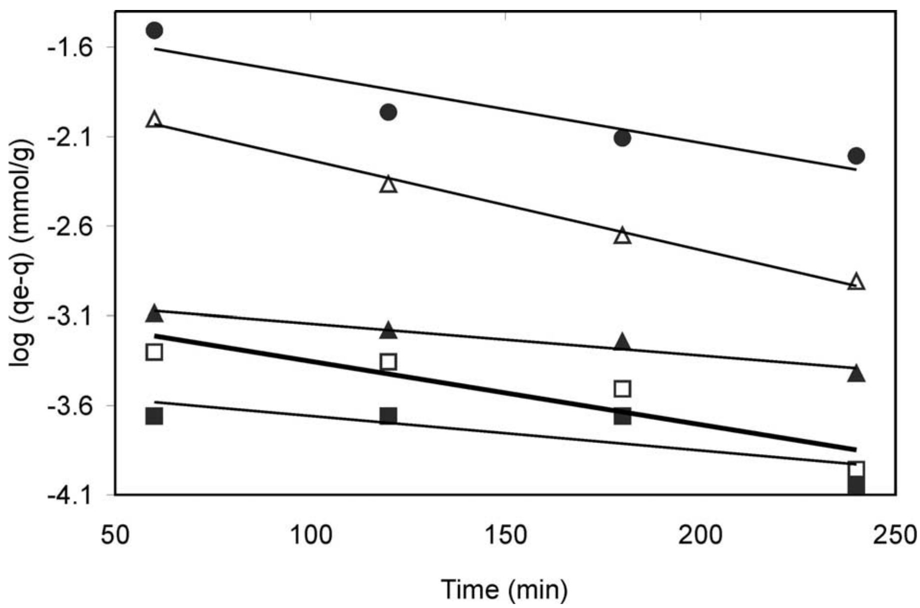


Fig. 2. Lagergren plots for adsorption of Brilliant Green at 300 K on a NLP dose of 0.63 g dm^{-3} (the curves from bottom to top represent initial dye concentrations of 2.07×10^{-2}, 4.14×10^{-2}, 6.23×10^{-2}, 8.29×10^{-2}, and 10.36×10^{-2} mmol dm^{-3}).

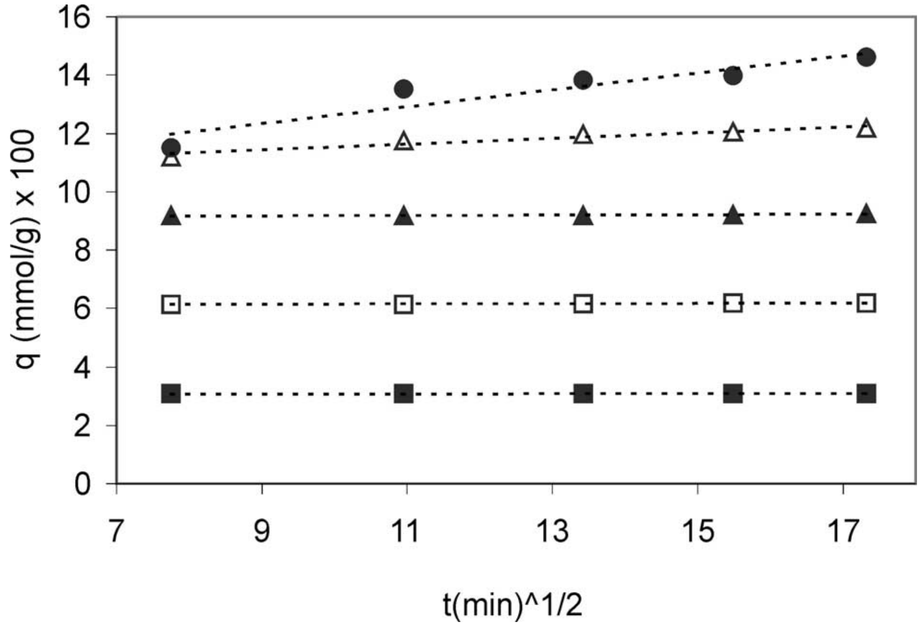


Fig. 3. The q_t vs. $t^{1/2}$ plots for adsorption of Brilliant green at 300 K on a NLP dose of 0.63 g dm^{-3} (the curves from bottom to top represent initial dye concentrations of 2.07 × 10^{-2}, 4.14 × 10^{-2}, 6.23 × 10^{-2}, 8.29 × 10^{-2}, and 10.36 × 10^{-2} mmol dm^{-3}).

slow compared to the initial rate of adsorption. Intra-particle diffusion rate constant in the range 0.81–2.42 mg g^{-1} $min^{-1/2}$ for adsorption of methyl orange, methylene blue, and rhodamine B on banana and orange peel powder has been recently reported [24]. These values are higher than what is found in the present work. On the other hand, for the same work, the first order adsorption rate constant was found in the range 0.19–0.40 min^{-1} [24], while the present work of adsorption of Brilliant Green on NLP yielded a rate constant of only 7.32 × 10^{-3} min^{-1}. The uptake of the dye by NLP and its diffusion into the interior is a slow process governed by the transport processes of the dye molecules from the liquid phase to inside the pores of the NLP particles. It may be concluded therefore that the mechanism of adsorption of the dye, Brilliant green on NLP can be described as proceeding through a comparatively fast first order adsorption on external surface of the NLP particles followed by a slow diffusion into the interior of the pores of the particles. Identical mechanisms have been suggested by various workers for adsorption of different dyes on a variety of adsorbents [34,35].

For a fixed NLP dose, an increase in dye concentration resulted in a decrease in the percentage adsorption of the dye (Table 2). This is more prominent at lower NLP doses. With a NLP dose of 0.13 g dm^{-3}, the adsorption decreased from 84.0 to 55.8% in the dye concentration range of 2.07–10.4 × 10^{-2} mmol dm^{-3}, but at a NLP dose of 0.63 g dm^{-3}, the decrease was only from 99.5 to 78.3% in the same concentration range. However, if amount adsorbed (mmol) per unit mass (g) of the adsorbent is taken into consideration, there is a steady increase in adsorption with increasing dye concentration. This is shown in Fig. 4. The results have indicated that by suitably adjusting the adsorbent dose, it is possible to bring about 100% removal of the dye Brilliant Green through the process of adsorption. The uptake of the dye increases at a faster rate for a higher concentration of the dye if the adsorbent dose is increased. For example, chemically treated and powdered Psidium Guyava Leaves can remove 100% of the dyes methylene blue and crystal violet from aqueous solution if the dosage is 2 g dm^{-3} [32]. Such high dose is not required in the present case.

Table 2
Percentage adsorption data of Brilliant Green on Neem leaf powder at 300 K for a contact time of 4 h

Dye concentration		Percentage adsorption of the dye on NLP dose of				
mg dm^{-3}	(mmol dm^{-3})	0.13 g dm^{-3}	0.27 g dm^{-3}	0.4 g dm^{-3}	0.53 g dm^{-3}	0.63 g dm^{-3}
10	2.07×10^{-2}	84.0	90.0	95.0	98.8	99.5
20	4.14×10^{-2}	80.0	84.5	93.0	98.2	99.2
30	6.22×10^{-2}	75.5	79.5	90.0	97.8	98.8
40	8.29×10^{-2}	69.5	74.0	85.0	90.5	97.0
50	10.36×10^{-2}	55.8	59.7	68.4	76.0	78.3

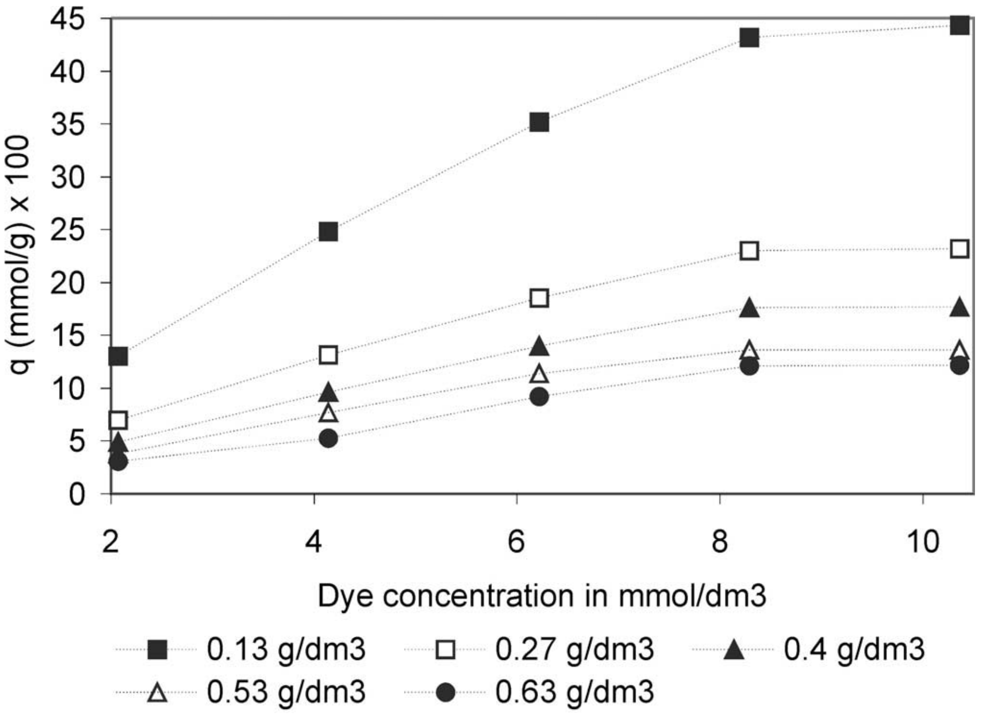


Fig. 4. Variation of amount adsorbed with dye concentration at different NLP doses for adsorption of Brilliant Green on Neem Leaf Powder at 300 K.

Adsorption of the dye on NLP yielded good fits with the Langmuir isotherm as well as the empirical Freundlich Isotherm. The isotherm plots are shown in Figs. 5 and 6. In all cases, the correlation coefficient shows excellent agreement with the theoretical equations. The Langmuir plots (Fig. 5) obtained for different NLP doses at five different dye concentrations almost converged towards the C_e/q_e axis indicating that they had widely differing slopes, but similar intercepts. This is also reflected in the values of the Langmuir coefficients obtained from these plots (Table 3). The monolayer capacity (C_1) varied from 0.149 to 0.554 mmol g^{-1}. These values are much larger than the values obtained for adsorption of the dyes, safranine and methylene blue, on various low cost adsorbents [23] showing the potentiality of the NLP as an adsorbent. The monolayer capacity values obtained in this work are also considerably larger than a few reported values [7,24] obtained for

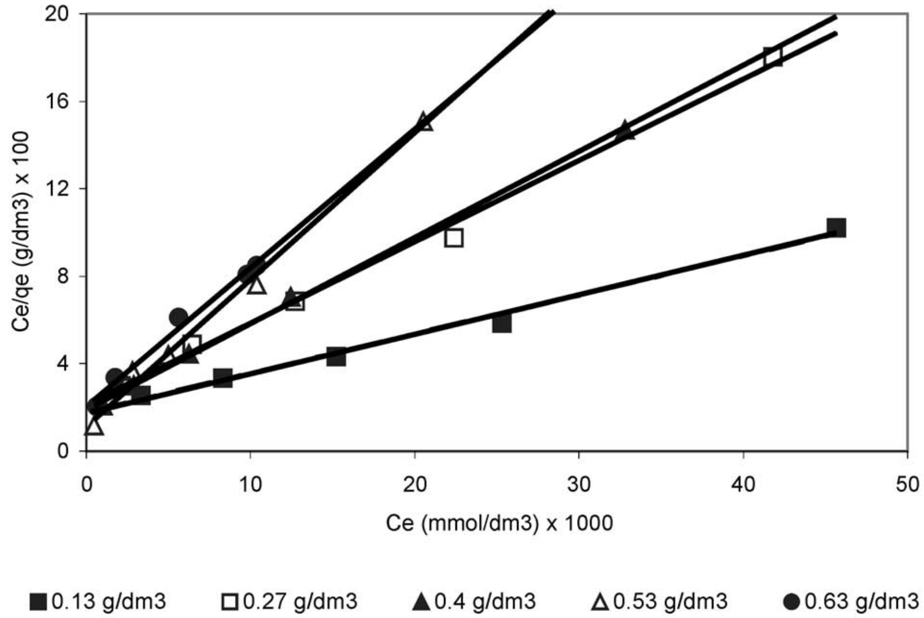


Fig. 5. Langmuir isotherm plots for adsorption of Brilliant Green on Neem leaf powder at 300 K at different adsorbent doses with dye concentrations of 2.07×10^{-2}, 4.14×10^{-2}, 6.23×10^{-2}, 8.29×10^{-2}, and 10.36×10^{-2} mmol dm^{-3} for each dose.

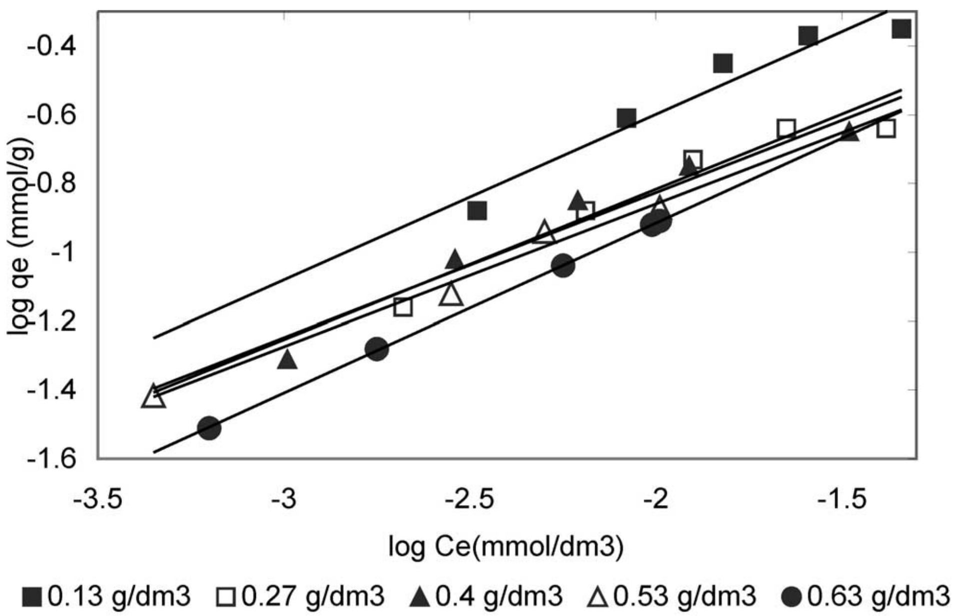


Fig. 6. Freundlich isotherm plots for adsorption of Brilliant Green on Neem leaf powder at 300 K at different adsorbent doses with dye concentrations of 2.07×10^{-2}, 4.14×10^{-2}, 6.23×10^{-2}, 8.29×10^{-2}, and 10.36×10^{-2} mmol dm^{-3} for each dose.

Table 3
Freundlich and Langmuir coefficients for adsorption of the dye, Brilliant Green on Neem leaf powder at 300 K[a]

NLP (g dm^{-3})	Freundlich coefficients			Langmuir coefficients			
	R	n	K_f (dm^3 g^{-1})	R	C_1 (mmol g^{-1})	K_d (dm^3 mmol^{-1})	R_L
0.13	0.96	0.49	2.36	0.99	0.554	1.046	0.939
0.27	0.97	0.42	1.04	0.99	0.269	1.725	0.903
0.40	0.98	0.43	1.12	0.99	0.254	2.070	0.885
0.53	0.96	0.42	1.07	0.99	0.149	5.981	0.728
0.63	0.99	0.49	1.17	0.99	0.158	3.089	0.838
Mean	0.97	0.45	1.35	0.99	0.277	2.782	0.859

R, linear regression coefficient.
[a] Contact time of 4 h, dye concentration of 2.07, 4.14, 6.22, 8.29, and 10.36 × 10^{-2} mmol dm^{-3}.

adsorption of a number of dyes on powdered banana and orange peels. The NLP particles are likely to have a very good number of adsorption sites to hold the dye molecules. The other Langmuir coefficient, K_d, related to the dye–NLP equilibrium has also values in the range 1.046–5.981 dm^3 mmol^{-1} indicating the equilibrium to have shifted appreciably towards formation of the adsorbed states on the NLP surface. The dimensionless parameter, R_L, has values from 0.728 to 0.939. These values show that the adsorption of the dye, Brilliant Green on the adsorbent, NLP can be exploited for practical application.

The Freundlich isotherm plots (Fig. 6) are nearly parallel to one another and they yield very close values for the coefficient, n (range 0.42–0.49). With these values <1.0, the Freundlich plots further demonstrate favourable adsorption of the dye on NLP. The values of the correlation coefficient demonstrate almost perfect agreement of the experimental data with the Freundlich equation. This, however, is indicative of the heterogeneity of the adsorption sites on the NLP particles. The other Freundlich coefficient, K_f has values in the range 1.04–2.36 dm^3 g^{-1}. These values of the adsorption coefficients obtained in the present work agree closely with those obtained for adsorption of as many as six different dyes on orange and banana peel powder [24].

The equilibrium thermodynamic data for the adsorption of the dye on NLP are presented in Table 4. The parameters ΔH^o, ΔS^o, ΔG^o were computed from the plots of log q/C_e vs. $1/T$ (Fig. 7). The enthalpy of adsorption in the temperature range, 300–323 K, for five different dye concentrations, varied between 5.66–17.64 kJ mol^{-1} with a mean value of 12.12 kJ mol^{-1}. The adsorption interaction is endothermic in nature, but the required activation enthalpy is not very large. The endothermic nature is also shown by the increase in the amount of adsorption with rising temperature as shown in Fig. 8. The increase

Table 4
Thermodynamic parameters for adsorption of the dye, Brilliant Green on Neem Leaf Powder (0.4 g/dm^3) after a contact time of 4 h

Dye concentration (mmol dm^{-3})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	$-\Delta G^0$ (kJ mol^{-1}) at temperature			
			300 K	303 K	313 K	323 K
2.07 × 10^{-2}	5.66	42.69	7.15	7.28	7.70	8.13
4.14 × 10^{-2}	10.76	60.18	7.30	7.48	8.08	8.68
6.22 × 10^{-2}	9.08	56.81	7.96	8.13	8.70	9.27
8.29 × 10^{-2}	17.47	86.46	8.48	8.74	9.60	10.47
10.36 × 10^{-2}	17.64	88.97	9.05	9.32	10.21	11.10
Mean	12.12	67.02	7.99	8.19	8.86	9.53

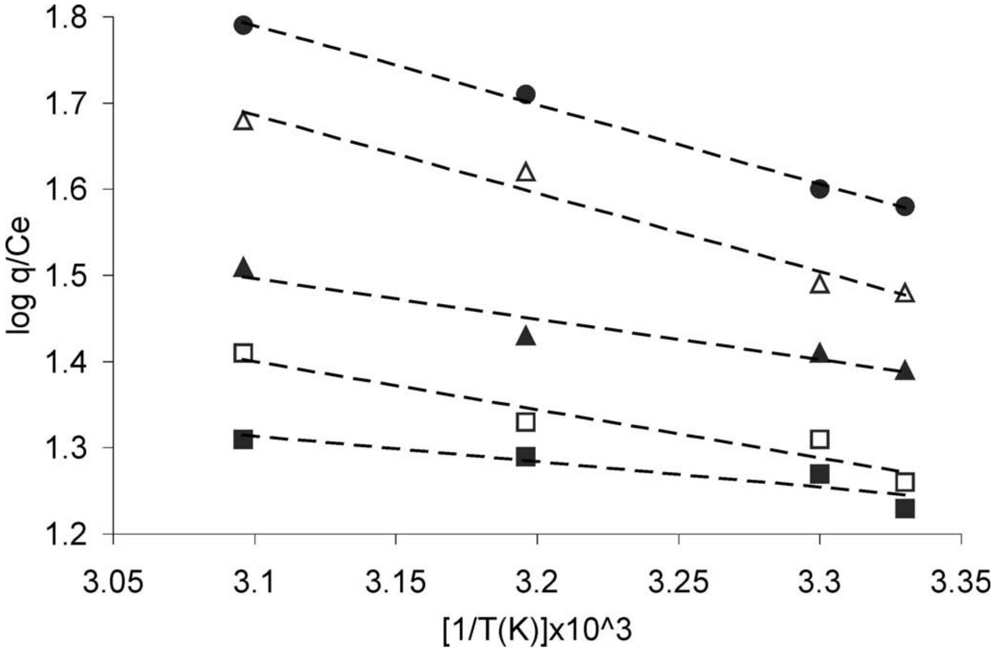


Fig. 7. Plots of log (q/C_e) vs. $1/T$ for adsorption of Brilliant Green on Neem Leaf Powder with dye concentrations of 2.07×10^{-2}, 4.14×10^{-2}, 6.23×10^{-2}, 8.29×10^{-2}, and 10.36×10^{-2} mmol dm^{-3} (from bottom to top) for NLP dose of 0.27 g dm^{-3} and contact time of 4 h.

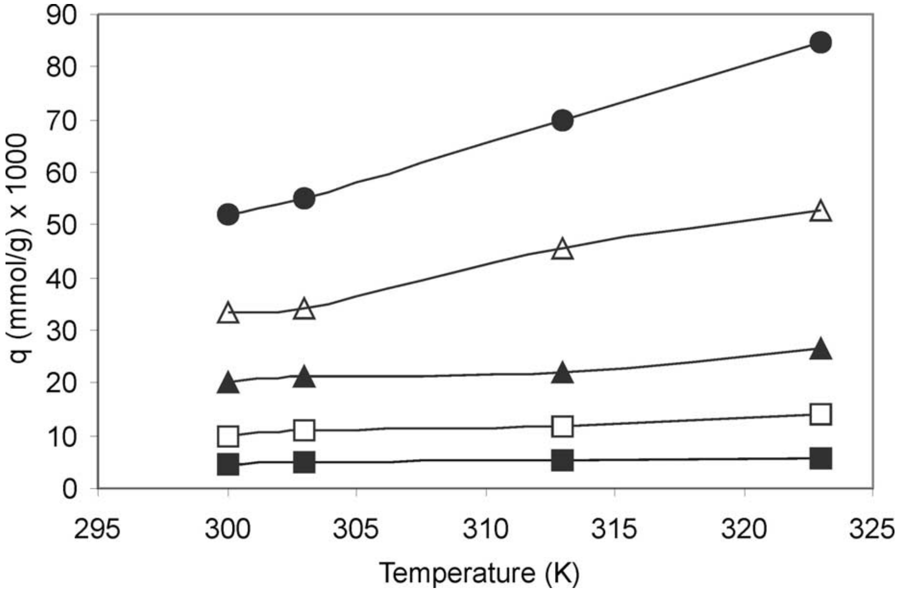


Fig. 8. Variation of amount adsorbed with temperature for adsorption of Brilliant Green on Neem leaf powder at dye concentrations of 2.07×10^{-2}, 4.14×10^{-2}, 6.23×10^{-2}, 8.29×10^{-2}, and 10.36×10^{-2} mmol dm^{-3} (from bottom to top).

was much more prominent for higher dye concentrations. The adsorption is accompanied by an increase in entropy of 61.02 J mol^{-1} K^{-1} (mean value), which shows that the adsorbed dye molecules on NLP surface are organized in a much more random fashion compared to the situation in the aqueous phase. The Gibbs energy change for the adsorption process is not very large, but its negative values indicate that the equilibrium,

$$\text{Brilliant Green} + \text{NLP} = \text{Brilliant Green} \cdots \text{NLP}$$

shifts to the right hand direction in a spontaneous manner leading to binding of the dye molecules to the NLP particles.

Endothermic adsorption of some dyes on various adsorbents has been reported earlier. The adsorption of methylene blue and malachite green on chemically treated Psidium Guyava leaves [32] was found to be endothermic with enthalpy of adsorption values of 7.35 and 4.00 kJ mol^{-1}. A detailed study of methylene blue adsorption on kaolinite also indicated the process to be endothermic with ΔH^{o} values of 6.03–13.53 kJ mol^{-1} [36]. These results are in agreement with the present work.

4. Conclusion

The dye Brilliant Green adsorbs very well on a non-conventional adsorbent such as powdered dry leaves of the Neem tree. The adsorption experiments were conducted in the concentration range of 2.07×10^{-2} to 10.36×10^{-2} mmol dm^{-3} at four different temperatures of 300, 303, 313 and 323 K with adsorbent dose of 0.13–0.63 g dm^{-3}. Even after a contact time of just 1 h, an amount of the adsorbent as small as 0.13 g dm^{-3} could remove nearly 25% of the dye from an aqueous solution containing 40 mg of the dye in 1 dm^{-3}, the adsorption increasing to 71.8% after 5 h. If the adsorbent dose was increased to 0.63 g dm^{-3}, the removal of the dye further increased to 98%. Studies of kinetics, adsorption isotherms and thermodynamics of the dye–adsorbent interactions show the potential of the NLP as a scavenger for dyes and pigments from water as a method of tertiary treatment of industrial effluents. The adsorption of the dye, Brilliant Green, was found to be endothermic indicating that the adsorption would be enhanced if the temperature of adsorption was a little above the ambient temperature. However, adsorption at ambient temperature was also substantial. The values of the adsorption coefficients, calculated from Langmuir and Freundlich equations agree well with the conditions of favourable adsorption.

References

[1] Chattopadhyay RR, Chattopadhyay RN, Maitra SK. Possible mechanism of anti-inflammatory activity of Azadirachta indica leaf extract. Indian J Pharmacol 1993;25: 99–100.

[2] Rawat NS. Neem plantation for better pesticides for reducing poverty and for protecting environment in India. Indian J Environ Protection 1994;14:433–9.

[3] Venugopal PV, Venugopal TV. Antidermatophytic activity of neem (Azadirachta indica) leaves in vitro. Indian J Pharmocol 1994;26:141–3.

[4] Majumdar AM, Upadhyay AS, Pradhan AM. Effect of Azadirachta Indica leaf extract on carbontetrachloride-induced hepatic damage in albino rats. Indian J Pharm Sci 1998;60:363–7.

[5] Chopra RN, Nayer SL, Chopra IC. Glossary of Indian medicinal plants. New Delhi: C.S.I.R; 1956, p. 31.

[6] Wali N, Dhavan S, Garg S, Upadhyay SN. Anti-inflammatory effect of Neem leaf extract. In: Proceedings of World Neem Conference, Bangalore, India, 1993.

[7] Sivraj R, Namasivayam C, Kadirvelu K. Orange peel as an adsorbent in the removal of Acid Violet 17(acid dye) from aqueous solution. Waste Management 2001;21:105–10.

[8] An H, Xiasheng Q, Yi G, Tang WZ. Biological treatment of dye wastewaters using an anaerobic–oxic system. Chemosphere 1996;33:2533–42.

[9] Liakou S, Pavlou S, Lyberatos G. Ozonation of azo dyes. Water Sci Technol 1997;35:279–86.

[10] Sarasa J, Roche MP, Ormad MP, Gimeno E, Puig A, Ovelleiro JL. Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. Water Res 1998;32:2721–7.

[11] McKay G, Otterburn MS, Aga DA. Fullers earth and fired clay as adsorbent for dye stuffs. Equilibrium and rate constants. Water, Air and Soil Pollution 1985;24: 307–22.

[12] Dutta PK. An overview of textile pollution and its remedy. Indian J Environ Protection 1994;14:443–6.

[13] Gregory AR, Elliot S, Kluge P. Ames testing of direct black 3B parallel carcinogenecity. J Applied Toxicol 1991; 1:308–13.

[14] Walker GM, Weatherley LR. Adsorption of acid dyes onto granular activated carbon in fixed beds. Water Res 1997;31:2093–101.
[15] Walker GM, Weatherley LR. Fixed bed adsorption of acid dyes onto activated carbon. Environ Pollut 1998;99:133–6.
[16] Chern Jia-Ming, Wu Chia-Yuan. Desorption of dye from activated carbon beds: effects of temperature, pH, and alcohol. Water Res 2001;35:4159–65.
[17] Nawar SS, Doma HS. Removal of dyes from effluents using low cost agricultural byproducts. Sci Total Environ 1989;79:271–9.
[18] Pollard SJT, Fowler GD, Sollars CJ, Perry R. Low cost adsorbents for water and waste water treatment: a review. Sci Total Environ 1992;116:3331–52.
[19] Nassar MM, Hamoda MF, Radwan GH. Adsorption equilibria of basic dyestaff on to palm-fruit bunch particles. Water Sci Technol 1995;32:27–32.
[20] Namasivayam C, Muniasamy N, Gayatri K, Rani M, Ranganathan K. Removal of dyes from aqueous solutions by cellulosic waste orange peel. Bioresource Technol 1996; 57:37–43.
[21] Ramakrishna KR, Viraraghavan T. Dye removal using low cost adsorbents. Water Sci Technol 1997;36:189–96.
[22] Ho YS, Mckay G. Sorption of dye from aqueous solution by pit. Chem Eng J 1998;70:115–24.
[23] Mckay G, Porter JF, Prasad GR. The removal of dye colour from aqueous solutions by adsorption on low-cost materials. Water, Air and Soil Pollution 1999;114:423–38.
[24] Annadurai Gurusamy, Juang Ruey-Shin, Lee Duu-Jong. Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. J Hazard Mater 2002;B92:263–74.
[25] Namasivayam C, Kavitha D. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes and Pigments 2002;54:47–58.
[26] Dutta M. Adsorption of certain beta-lactam antibiotics on activated carbon/polymeric resins: equilibrium and kinetic studies. PhD.thesis, Gauhati University, India, 1999 [unpublished].
[27] McKay G. Adsorption of dyestuff from aqueous solutions with activated carbon 1: equilibrium and batch contact time studies. J Chem Tech Biotechnol 1982;32:759–72.
[28] Hall KR, Eagleton LC, Acrivos A, Vermeulen T. Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. Ind Eng Chem Fund 1966;5:212–9.
[29] Khan SA, Rehman R, Khan MA. Adsorption of Cr (III), Cr (VI) and Ag (I) on Bentonite. Waste Mgmt 1995;15: 271–82.
[30] Namasivayam C, Ranganathan K. Removal of Cd(II) from wastewater by adsorption on waste Fe(III)/Cr(III) hydroxide. Water Res 1995;29:1737–44.
[31] Balasubramanian N, Ahamed AJ. Adsorption dynamics—determination of activation parameters for the adsorption of Pb(II) on to lignite material. Pollut Res 1998;17:341–5.
[32] Singh DK, Srivastava B. Removal of basic dyes from aqueous solutions by chemically treated Psidium guyava leaves. Indian J Environ Hlth 1999;41:333–45.
[33] Weber WJ, Morris JC. Kinetics of adsorption on carbon solution. J San Eng Div ASCE 1963;89:31–59.
[34] McKay G. Adsorption of dyestuffs from aqueous solutions using activated carbon. J Chem Technol Biotechnol 1983;33A:196–204.
[35] Wu Feng-Chin, Tseng Ru-Ling, Juang Ruey-Shin. Comparative adsorption of metal and dye on flake- and bead-types of chitosans prepared from fishery wastes. J Hazard Mater 2000;B73:63–75.
[36] Ghosh D, Bhattacharyya KG. Adsorption of methylene blue on kaolinite. Appl Clay Sci 2002;20:295–300.