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Research Article

Kinetic and Thermodynamic Studies on the Adsorption Behavior of Naphthol Green B Dye Using Casuarina Equisetifolia Bark Carbon

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Abstract: The adsorption behavior of Naphthol Green B dye from aqueous solution was investigated using Casuarina equisetifolia bark carbon. The effect of various experimental factors such as pH, adsorbent dose, initial dye concentration, contact time and temperature were studied by using the batch technique. The adsorption capacities were evaluated by using Langmuir and Freunlich adsorption isotherm models. Thermodynamic parameters were calculated and it was found that the adsorption of Naphthol Green B (NGB) dye using Casuarina equisetifolia bark carbon (CEBC) was endothermic and adsorption process. Pseudo first order, Pseudo second order and intra particle diffusion models were also used to describe the kinetic data.
Keywords: Adsorption, Kinetic, CEBC, NGB dye, Thermodynamic.

INTRODUCTION

The increase in population and rapid industrial growth in India has resulted in high demand for dyes and pigments [1]. Dyes are important pollutants in the effluents of textile, leather, food processing, cosmetics and paper manufacturing industries. The discharge of these dye wastes into receiving streams not only affects the aesthetic nature but also reduces photo-synthetic activity [2]. Waste waters offer considerable resistance for their biodegradation [4] and also a several commonly used have been reported to be carcinogenic and mutagenic for aquatic organisms [3]. Pollution caused by industrial waste water has become a common problem for many countries [5]. Therefore, it is necessary to reduce dye concentration in the waste water. Adsorption is an attractive and alternative for the treatment of waste water, especially if the adsorbent is inexpensive and does not require an additional pretreatment step before its application. Currently, the most commonly used adsorbent is activated carbon which will successfully remove the dyes from waste water [6, 7]. However, the activated carbon is considered to be an expensive and problem with regeneration of the spent activated carbon in its large scale application. In order to decrease the cost of water treatment, attempts have been made to find inexpensive low-cost adsorbents [8]. Therefore, new, economical, easily available and highly effective adsorbents still need to be found. The present study is used to find out the suitability of CEBC adsorbent to remove the Naphthol Green B from aqueous solution.

MATERIALS AND METHODS

Adsobate

Naphthol Green B (NGB) dye used in this study is purchased from Kevin Scientific Company. NGB has molecular formula $C_{30}H_{15}FeN_3Na_3S_3$. The dye stock solution was prepared by dissolving accurate weight of dye in distilled water to the concentration of 1g/L.

Preparation of Casuarina equisetifolia Bark Carbon (CEBC) adsorbent

Casuarina equisetifolia Bark Carbon (CEBC) was collected from local market. The collected CEBC materials were finely powder was treated with con. Sulphuric acid. The carbon was washed until an optimum pH and dried in hot air oven at 110°C for 24hours, then placed into muffle furnace at 450°C in 6 hours for complete carbonization of the bark. The resulting powder was used for adsorption experiment.

Batch method

Batch adsorption [9] studies were conducted in varying concentration of dye, adsorbent dose, contact time, temperature and pH. The concentration of dye used in the range of 8-40mg/L (8mg/L variation), adsorbent dose varied from 20 to 70 mg (10 mg variation), time varied in the range of 10-60 min (10 min intervals), temperature was varied in 303-333 K (10 K increment) and pH changed in the value of 2-9.The amount of adsorption q_t (mg/g) at time 't' , amount of adsorption at equilibrium q_e (mg/g),and % removal of NGB dye were calculated by

$$q_t=(C_o-C_t)V/W \quad (1)$$
$$q_e=(C_o-C_e)V/W \quad (2)$$
$$\% \text{ Removal}=[((C_O-C)_t/C_O) \text{ X } 100] \quad (3)$$

Where C_o (mg/L), C_t (mg/L) and C_e (mg/L) are the liquid phase concentration of NGB dye at initial, at particular time and equilibrium respectively. V (Litre) is the volume of the solution. W (gram) is the mass of dry adsorbent used.

RESULTS AND DISCUSSION

Effect of pH

The solution pH tremendously affected the nature and progression of the adsorption process. So it is essential to check the solution pH before proceeding to the adsorption process. In this study the solution pH was varied in the range of 2-9 and the effect of pH was presented in Fig.1. From the investigation of various pH values, the pH value of 4 shows the higher percentage removal compared to other pH values. Therefore the pH value of 4 was chosen as optimum pH for the removal of Naphthol green B on the Casuarina equisetifolia bark activated carbon.

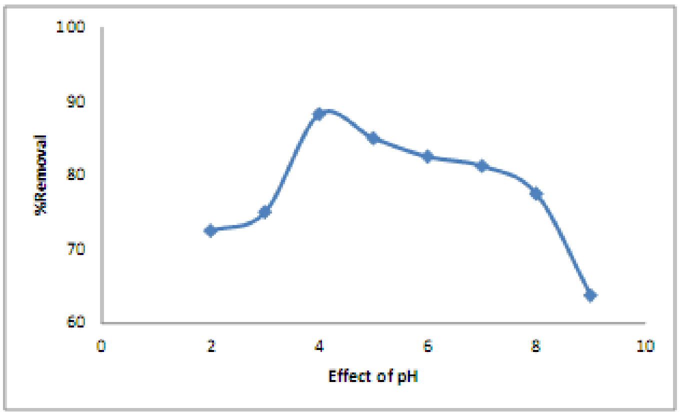

Fig-1: Effect of initial pH for the removal of NGB dye

Effect of CEBC adsorbent dose

To study the effect of CEBC dose on the NGB adsorption, different amounts of CEBC powder (20-70mg) were added into a 250ml conical flask containing a definite volume (25ml in the each flask)of fixed initial concentration (8mg/L) of dye solution without changing the pH of solution at 30̊C as shown in Fig .2. The flasks were placed in thermostatic orbital shaker for 60 minutes and the NGB dye concentrations were measured at equilibrium.

From the figure, it was observed that the % removal increase initially up to 50mg/25ml and reaches limiting value with fractional difference. Thus adsorption increase with an increase in the dose of adsorbent due to availability of more active sites for adsorption. However, a further increase in the dose of adsorbent did not affect the % removal of dye because of the unavailability of adsorbate due to saturation. So the experiments were carried out by using 50mg/25ml of adsorbent dose.

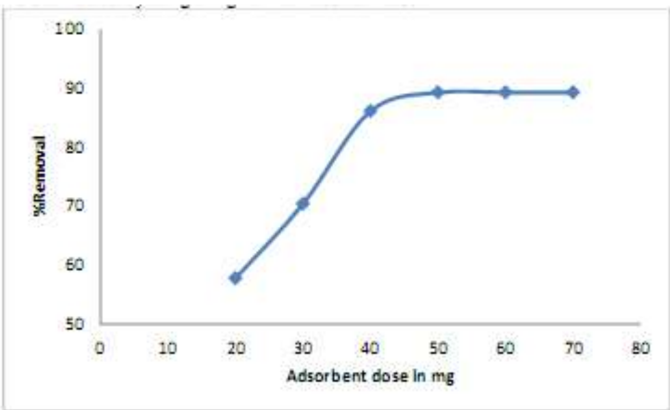

Fig-2: Effect of adsorbent dose for the removal of NGB dye

Effect of contact time

The effect of contact time between adsorbent CEBC and adsorbate (NGB) were determined by keeping NGB dye concentration, adsorbent dosage, pH and temperature were constant. In the present study, the adsorption process of NGB using CEBC was studied for various time intervals such as 10, 20,30,40,50 and 60 minutes. The results were presented in Fig .3.It was observed that initially increase in time enhances the rate of adsorption and its equilibrium was almost attained and 91.38% dye removal takes place within 40minutes.

Hereafter there was no appreciable change in adsorption. So, 40 minutes was the sufficient time for the maximum adsorption of dye.

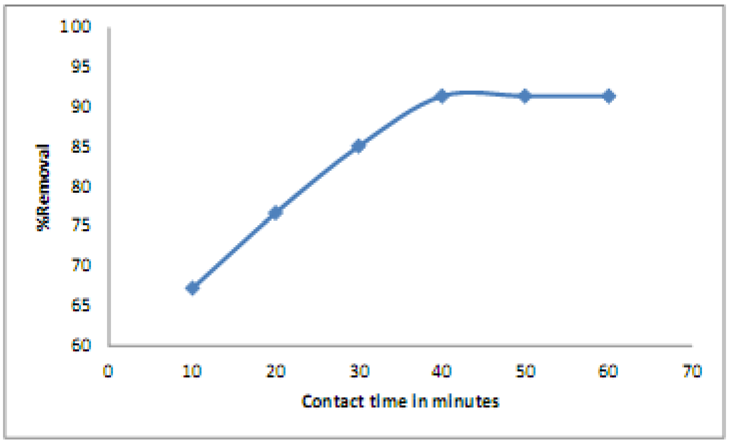

Fig-3: Effect of contact time for the removal of NGB dye

Effect of temperature

The effect of temperature was carried out at four different temperatures such as 30°C, 40°C, 50°C and 60°C in a thermostatic orbital shaker for 40 minutes. Samples were withdrawn at suitable time interval, filtrate was analyzed for the remaining dye concentration. Temperature has significant effects on the adsorption capacity, thermodynamic parameter and kinetic process depending on the structure and surface functional groups of an adsorbent.

ADSORPTION ISOTHERMS

The adsorption isotherm shows how the adsorbate molecules are distributed between the adsorbent and solution. The Langmuir and Freundlich isotherm were used to measure the adsorption capacity of the CEBC adsorbent for the removal of NGB dye.

Langmuir isotherm

The Langmuir [10] isotherm equation can be described by

$1/q_e=1/q_mK_LC_e+1/q_m$ (4)

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate per unit mass of adsorbent, q_m and K_L are Langmuir constants related to adsorption capacity and rate of adsorption respectively. q_m is the amount of adsorbate a complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and KL (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption. The linear plot of specific adsorption capacity $1/q_e$ against the equilibrium concentration ($1/C_e$) shows that the adsorption obeys the Langmuir model. The Langmuir constant q_m and K_L were determined from the slop and intercept of the plot. The equilibrium parameter RL [11] is used to find out the feasibility of the Langmuir isotherm

$R_L=1/1+K_LCo$ (5)

Where Co (mg/L) is the initial concentration of adsorbate and KL (L/mg) is Langmuir isotherm constant. The RL value between 0<RL<1 is favorable for adsorption.

Freundlich isotherm

Freundlich isotherm [12] is represented by the equation

$\log q_e = \log K_f + 1/n \log C_e$ (6)

Where q_e is the amount of dye adsorbed per unit weight of the adsorbent (mg/L), K_f is $[mg/g(mg/L)^{-1/n}]$ measure of adsorption capacity and 1/n is the adsorption intensity. In general if K_f value increases then adsorption capacity for a given adsorbate increases. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The adsorption is linear; if n<1, it implies that the adsorption process is favored by chemisorption and if n>1, the adsorption process is favored by physisorption.

Table 1: Adsorption isotherm parameter for the adsorption of NGB dye

Langmuir parameter			Freundlich parameter		
q_m(mg/g)	K_L(L/mg)	R^2	$K_F((mg/g)(l/mg)^{1/n})$	n(g/L)	R^2
16.393	97.230	0.9967	1.897	1.970	0.9856

Adsorption kinetics

The rate constant for the adsorption of NGB was determined using pseudo first order, pseudo second order, and intra particle diffusion models.

Pseudo first order equation

The adsorption kinetic data were described by the pseudo first order model which is the earliest known equation, described the adsorption rate based on the adsorption capacity. The pseudo second order rate equation can be written as [13].

$$\log (q_e-q_t)=\log qe-t.k_1/2.303 \qquad (7)$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/L), q_t is the amount of dye adsorbed (mg/g) at time t, K_1 is the rate constant (min^{-1}) of the pseudo first order.

Pseudo second order equation

The pseudo second order [14] rate expression is represented as

$$t/q_t=1/h+1/q_e \times t \qquad (8)$$

Where ($mg/g^{-1}min^{-1}$) is the initial adsorption rate at t→0 and K is the rate constant of the pseudo second order kinetic equation ($gmg^{-1}min^{-1}$). The plot of t/q_t versus t is shown in Figure. The q_e, k and h can be determined from the slop and intercept of the plot, respectively, and are listed in Table 2.

Intra-particle diffusion model

The possibility of intraparticle diffusion [15] was explored by using intraparticle diffusion model, which is commonly expressed by the following equation

$$q_t=Kpt^{1/2}+C \qquad (9)$$

Where C is the intercept and K_p is the intraparticle diffusion rate constant ($mg/gmin^{1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$, Figure. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater will be the contribution of the surface adsorption in the rate controlling step. The calculated intraparticle diffusion coefficient K_p, C and R^2 values are listed in Table 2.

Table 2: Adsorption kinetic parameter for the adsorption of NGB dye

Pseudo first order			Pseudo second order			Intraparticle		
$K_{ad}(min^{-1})$	q_e(mg/g)	R^2	q_e(mg/g)	$h(mgg^{-1}min^{-1})$	R^2	$k_p(mg/g\ min^{1/2})$	C	R^2
0.0677	3.431	0.9735	3.954	0.7935	0.9984	0.2267	2.0392	0.9274

Thermodynamic studies

Table 3: Thermodynamic parameter for the adsorption of NGB dye

T(K)	ΔG^0 (KJ mol^{-1})	ΔH^0(KJ mol^{-1})	ΔS^0(KJ mol^{-1} k^{-1})
303	**-5.436**	**34.533**	**156.03**
313	**-6.201**		
323	**--7.159**		
333	**-7.378**		

The effect of temperature on the adsorption process was investigated with the thermodynamic parameter like change in Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS). The thermodynamic parameter values were presented in Table. From Table 3, the Gibbs free energy (ΔG) shows negative sign of an experimental value intimates that the process is spontaneous in nature. The reduction of the negative value at higher temperatures reveals that the equilibrium quantity reduces at higher temperatures. The positive value of change in enthalpy (ΔH) indicates that the endothermic nature of the process involved during the adsorption, moreover an interaction between the solute and the solvent particle involves in complex phenomenon on the solid surface. The change in entropy (ΔS) provides positive value implies that the conscious choice of an adsorbent raises with the increment of an orderliness between the adsorbate and the adsorbent molecules. From the results we may conclude that the adsorption of Naphthol Green B on Casuarina equisetifolia bark carbon was feasible.

CONCLUSION

The results of this study show that the Casuarina equisetifolia Bark Carbon can be used for the removal of the dyes Naphthol Green B from aqueous solution. The equilibrium data were fitted to the Langmuir and Freunlich models. The kinetics of the adsorption process was the best fit with pseudo second order and intraparticle diffusion model. This adsorption studies shows that Casuarina equisetifolia Bark Carbon can be used as an efficient adsorbent for the removal of Naphthol Green B dyes from aqueous solution. The thermodynamic studies indicate that adsorption process is edothermic and physical adsorption.

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