

Removal of Azure B Dye from Aqueous Solution by Adsorption onto Base of Palm Leaf: Thermodynamic and Kinetic Analysis

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Published online: 24 December 2014; AJC-16445

In the present study, locally base of palm leaf was used as a natural adsorbent for removing of textile dye (azure B) from aqueous solution. The effect of initial dye concentration, contact time, weight of adsorbent and temperature (25, 35 and 50 °C) were investigated. The per cent of dye removal increased with increasing base of palm leaf mass and the adsorption process was reached equilibrium after 60 min. The adsorption isotherms are of H-type according to Gile's classification. The calculated data were analyzed using Langmuir, Freundlich and Dubinin-R isotherms, the results show that the adsorption process was better described by Langmuir isotherm than the other isotherms. Langmuir constants were also calculated. The basic thermodynamic functions were evaluated (ΔH , ΔG , ΔS) and it was found that interaction of dye with the surface was exothermic and spontaneous. The adsorption mechanism and the nature of interaction between surface and azure B dye was studied by using FTIR spectroscopy. Pseudo-first order and pseudo-second order models were applied to experimental data at all temperatures (25, 35 and 50 °C), the adsorption followed pseudo-second order rate expression and the intraparticle diffusion may plays a role in the adsorption process. The activation energy of process was determined as 46.36 kJ/mol at 298 K. The adsorption of dye on base of palm leaf surface may be chemisorption in nature as indicated from desorption experiment.

Keywords: Removal, Azure B, Palm leaf.

INTRODUCTION

The main source of water pollution comes from wastewater which contains industrial and environmental pollutants¹. Dyes are widely distributed as environmental pollutants due to their presence in the wastewater of many industries such as, textile, rubber, paper, plastic and dye manufacturing industries²⁻⁴. Most of the used dyes are carcinogenic and mutagenic for aquatic life even in low concentrations⁵. The removal of dyes from effluents is of important but cannot be performed easily due to the synthetic origin and complex structure of dyes⁶.

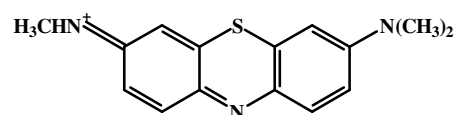
Various available technologies have been used to control water pollution such as, coagulation, foam flotation, ion exchange, sedimentation, chemical oxidation and adsorption^{7,8}. Adsorption process has a wider applicability in water pollution treatment due to low cost, convenience and simplicity of design⁹. Activated carbon has been widely used in wastewater treatment^{8,9}. A number of natural adsorbent materials have also been used for removal of dyes, such as rice husk¹⁰, tea waste¹¹, peanut hull¹², almond shell¹³, lemon peel¹⁴ and coir pith¹⁵.

The aim of the present work is to evaluate the capability of base of palm leaf surface for the removal of Azure B dye from aqueous solution, thermodynamic and kinetic analysis

were conducted to investigate the mechanism controlling adsorption process.

EXPERIMENTAL

Azure B was supplied by sigma; the chemical structure of this dye was shown in **Scheme-I**.



Scheme-I: Chemical structure of Azure B

Wavelength of maximum absorbency ($\lambda_{\max}$) was recorded for Azure B and found 646 nm (using UV-visible spectrophotometer, double beam, Shimadzu. PC 1650, Japan). This value was utilized for estimation of quantity of dye adsorbed. Solutions of different concentrations were prepared by serial dilution and the absorbance values of these solutions at 646 nm plotted against concentration values. The straight line obtained verifying the applicability of Beer-Lambert's law.

Preparation of surface: The base of palm leaf in powder form was washed with excessive amounts of distilled water;

to remove dust and soluble materials. Washed surface was then dried under sunlight and in an oven at 60 °C for 2 h and kept in airtight container.

Effect of weight of the adsorbent: Adsorption experiment was done at 25 °C, using different weights of adsorbent (0.01-0.2 g) in 10 mL solution containing fixed concentration of dye (60 ppm).

Adsorption isotherm: The adsorption isotherms were determined by shaking 0.1 g of base of palm leaf into 10 mL dye solutions, having concentrations ranging between 20-500 ppm at pH ≈ 7.4. After 60 min of shaking (using shaker water bath, K&K, Scientific, Korea), the suspensions were centrifuged at 3000 rpm for 15 min. The dye concentration was determined spectrophotometrically.

The quantity of Azure B dye adsorbed was calculated according to the following equation¹⁶:

$$q_e \text{ or } \frac{x}{m} = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where: x is the quantity adsorbed, m is the weight of adsorbent (g), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of solution (L).

Adsorption experiment was repeated in the same manner at 25, 35 and 50 °C to estimate the basic thermodynamic functions.

FTIR Analysis: The surface structure of base of palm leaf before and after dye sorption was analyzed by FTIR spectroscopy (FTIR spectrophotometer, Shimadzu.8500, Japan). IR absorbance data were recorded for wavenumbers in the range of 4000-400 cm^{-1} .

Kinetic studies: The effect of contact time was determined by adding 0.1 g of adsorbent into 10 mL dye solutions, with initial concentration 60 ppm under shaking. The temperature of solution was held constant at 25 °C with a thermostatic shaker. After different time intervals, the residual dye concentration was determined. The percentage of dye removal was calculated as follows:

$$\text{Removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Desorption studies: The elution extent of dye was determined using distilled water as elution media. Dye-loaded base of palm leaf sorbent was shaken with 10 mL portion of distilled water for 60 min at 25 °C. The suspensions were centrifuged and analyzed for dye desorbed.

RESULTS AND DISCUSSION

Effect of adsorbent weight: The influence of base of palm leaf mass on the percent removal of azure B dye was studied. As the weight of adsorbent is increased from 0.01 to 0.2 g, the percent removal efficiency of dye increased from 98.4 to 100 %, Fig. 1. An increase of mass of adsorbent increases the surface area and the number of available active sites for adsorption; therefore, the per cent of adsorbed dye increases.

Adsorption of dye: The adsorption of azure B dye from aqueous solution onto base of palm leaf has been studied at 25 °C and at other two temperatures 35 and 50 °C (Fig. 2).

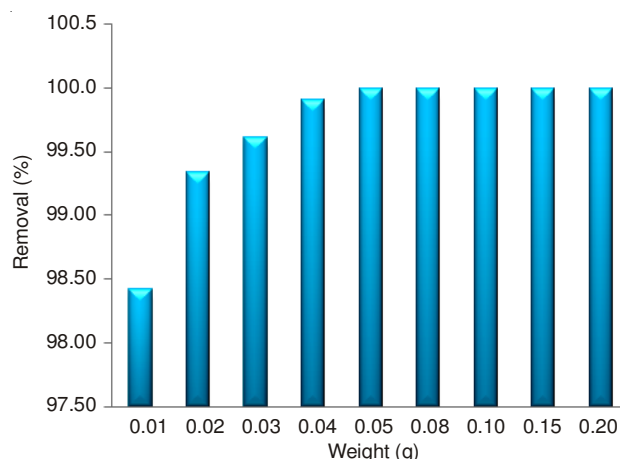


Fig. 1. Effect of adsorbent weight on the per cent removal of azure B at 25 °C

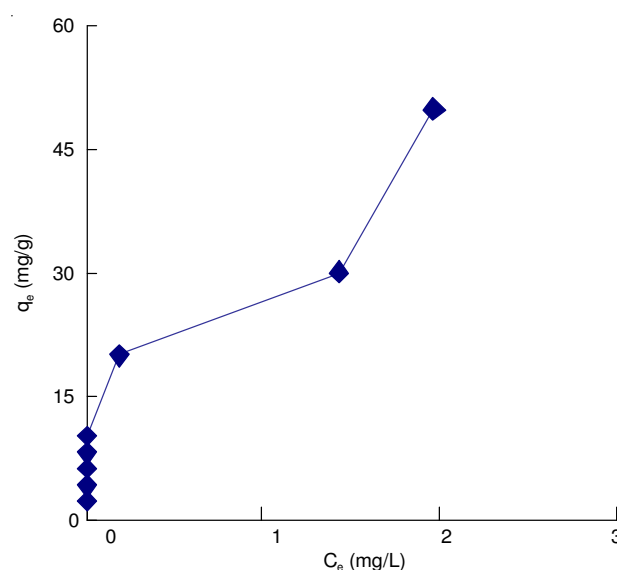


Fig. 2. Adsorption isotherm of azure B on base of palm leaf at pH 7.4 at 25 °C

The adsorption capacity of base of palm leaf surface increased with increasing initial dye concentration. The increase of dye concentration accelerates the mobility of dye molecules in the liquid phase, due to increase in the driving force of concentration gradient.

FTIR spectra of base of palm leaf surface before and after adsorption of Azure B dye are shown in Fig. 3.

The spectrum of base of palm leaf surface has broad absorption peak at wavenumbers 3500-3100 cm^{-1} , corresponding to the overlapping of -OH and -NH peaks. The peak at 2918 cm^{-1} represents the stretching vibration of alkyl groups and the peaks at 1735-1600 cm^{-1} can be attributed to C=O bands in carboxyl and amide groups^{17,18}. According to the information obtained from FTIR spectrum of the adsorbent, the base of palm leaf surface contains functional groups such as hydroxyl, carboxyl and amine groups. The intensity of some of these peaks decreased and shifted to different wavenumbers after adsorption of dye (Fig. 3-b). The broad absorption band at 3409 cm^{-1} shifted to 3379 cm^{-1} and the band at 1735 cm^{-1} that corresponds to C=O group shifted to 1720 cm^{-1} , suggesting the involvement of these groups in adsorption process.

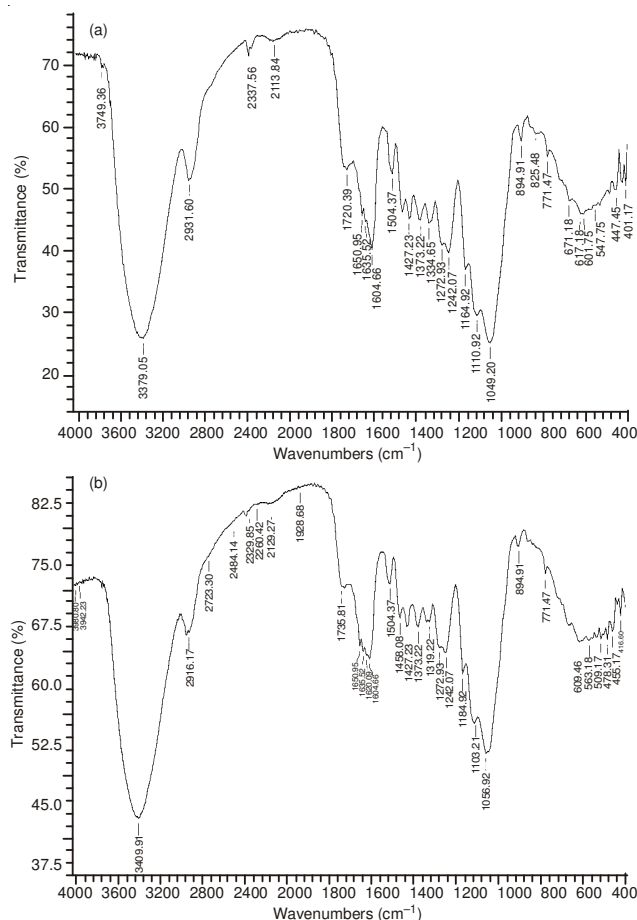


Fig. 3. FTIR spectra of base of palm leaf surface: (a) before and (b) after adsorption of azure B dye

Adsorption isotherm: The shapes of azure B isotherms can be considered as H-type according to Giles classification¹⁹. The H-type isotherm is attained when there high affinity between the adsorbate and the adsorbent surface.

The experimental data of adsorption isotherm were tested for their applicability to Langmuire, Freundlich and D-R models. The adsorption of azure B dye onto base of palm leaf, follows isotherm which are best represented by applying the langmuire equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \left(\frac{1}{q_m} \right) \cdot C_e \quad (3)$$

where q_e (mg/g) is the quantity adsorbed per unit weight, C_e (mg/L) is the equilibrium concentration, q_m (mg/g) and K_L (L/mg) are Langmuir isotherm constants.

Fig. 4, shows the linear plot of C_e/q_e versus C_e for the removal of azure B dye at 25 °C. The values of Langmuir constants and the correlation coefficient ($K_L = 18.55$, $q_m = 41.49$, $r^2 = 0.909$), indicate that the adsorption of dye follows the Langmuir model. The low values of correlation coefficients show that the Freundlich ($r^2 = 0.0044$) and D-R model ($r^2 = 0.64$) are less fitted to the adsorption process compared to Langmuir model.

Thermodynamic parameters: The adsorption extent of azure B on base of palm leaf decreased with the increase of temperature from 25 to 50 °C, indicate that the adsorption process was exothermic in nature (Fig. 5). This result could

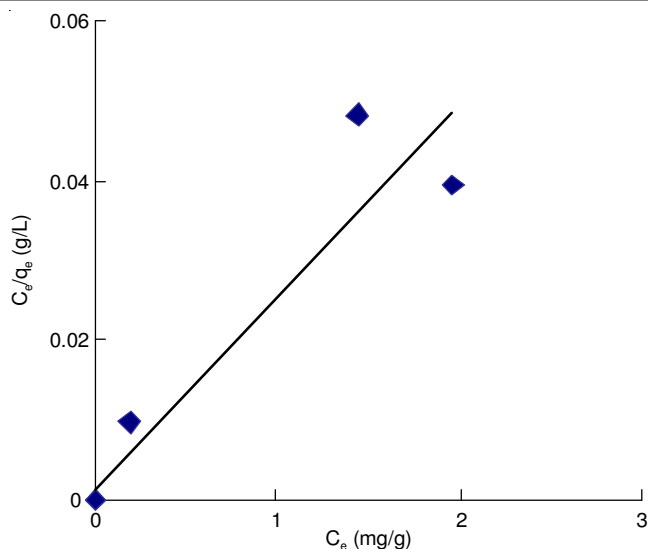


Fig. 4. Linear form of Langmuir isotherm of azure B on base of palm leaf

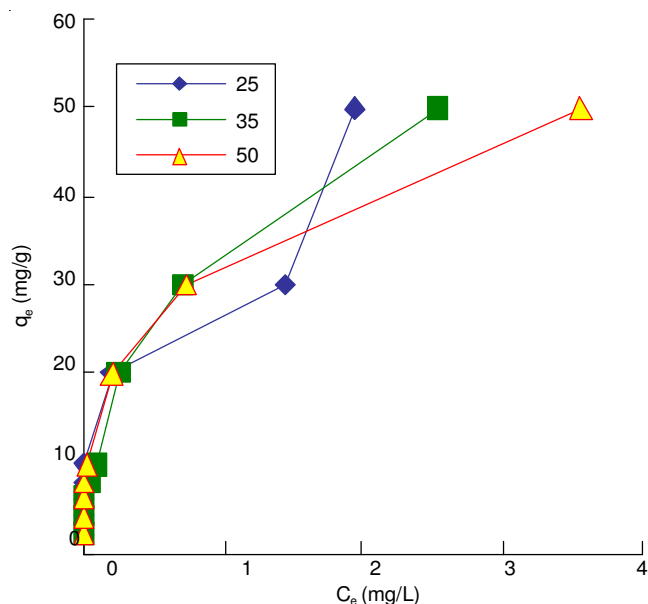


Fig. 5. Adsorption isotherms of azure B on base of palm leaf at different temperatures (°C)

be interpreted as a weakening of attractive forces between the dye molecules and the solid surface with the increase of temperature.

The thermodynamic parameters (ΔH , ΔG and ΔS) are calculated based on eqns. 4-6 (Table-1):

$$\ln X_m = \frac{-\Delta H}{RT} + \text{constant} \quad (4)$$

$$\Delta G = -RT \ln K \quad (5)$$

$$\Delta G = \Delta H - T \Delta S \quad (6)$$

The adsorption of azure B dye on base of palm leaf is exothermic in conjunction with an increase in entropy (Table-1). The positive value of entropy supported diffusion process of dye into the chemical structure of adsorbent²⁰. The free energy with negative value reflects the affinity of base of palm leaf surface for dye molecules and the adsorption process is spontaneous in nature.

TABLE-1
VALUES OF THERMODYNAMIC FUNCTIONS FOR
ADSORPTION OF AZURE B ON BASE OF PALM LEAF

ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	K
-7.944	-13.725	19.399	254.081

Kinetic analysis: The amount of azure B adsorbed and the percentage of dye removal as a function of time at different temperatures are shown in Fig. 6. The results show that the rate of dye removal increased with increasing temperatures from 25 to 50 °C.

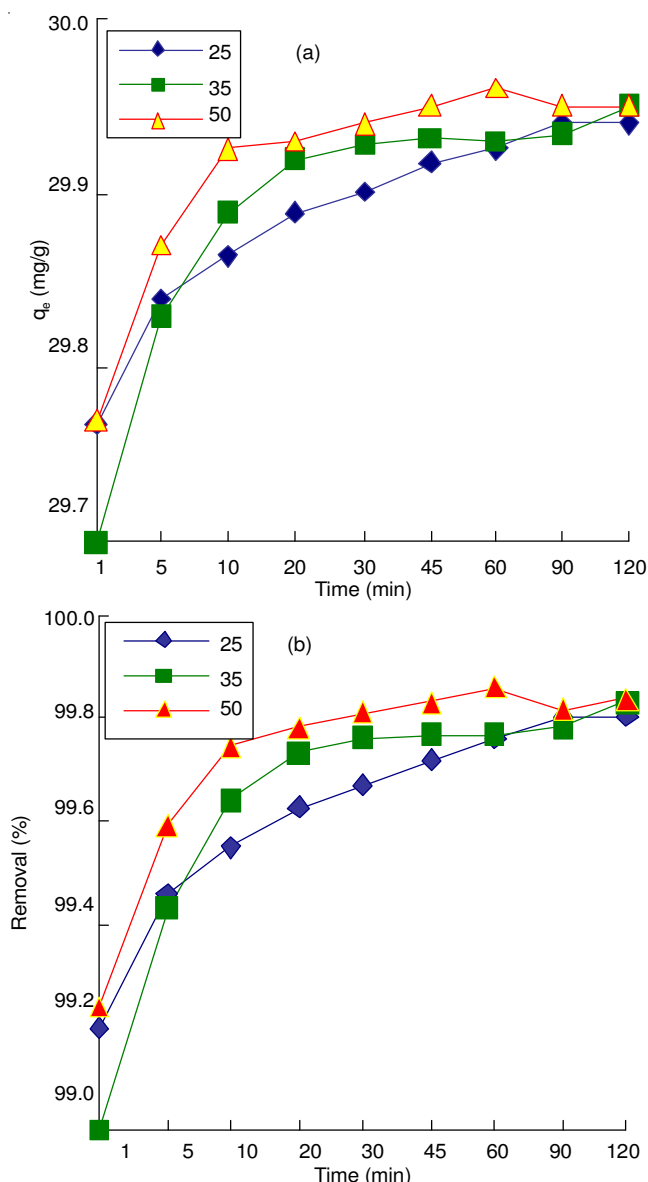


Fig. 6. Effect of contact time on the removal of dye at different temperatures (°C)

In the adsorption process, the initial uptake of dye is primarily attributed to the adsorption of dye molecules at the exterior surface of adsorbent until reached equilibrium. The rate of removal of dye from aqueous solution is controlled by the diffusion of dye molecules to the interior surface of the adsorbent. The interior surface seems to be very active and have a very high affinity towards dye molecules. So, the amount of dye uptake by adsorbent is increased²¹.

To predict the mechanism of adsorption and the adsorption kinetics of dye, pseudo-first order and pseudo-second order kinetic models were applied to experimental data. The linear form of pseudo-first order equation²² is expressed as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where q_e and q_t are amount of dye adsorbed (mg/g) at equilibrium and time t (min), respectively, k_1 is the rate constant of pseudo-first order kinetic. Values of k_1 for adsorption process of azure B dye on base of palm leaf at different temperatures were obtained from the slope of plot of $\ln (q_e - q_t)$ vs. t (Fig. 7).

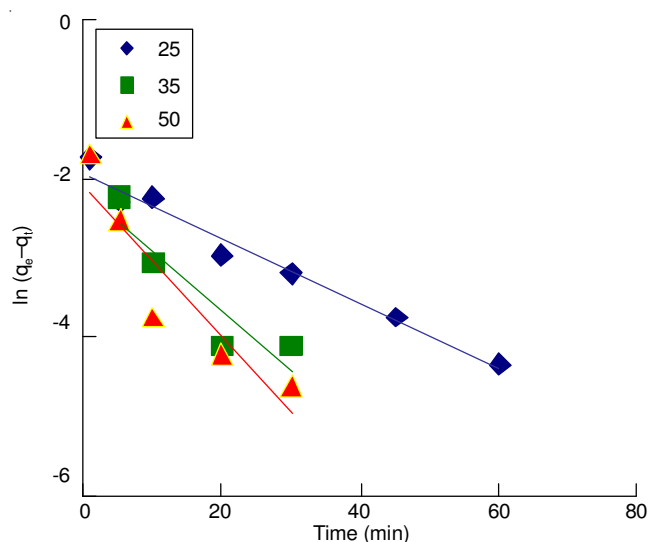


Fig. 7. Applicability of pseudo-first order kinetic model to dye adsorption

The pseudo-second order kinetic model²³ is:

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

where h is the initial adsorption rate and is equal to: $h = k_2 q_e^2$; k_2 is the pseudo-second order rate constant. The plot t/q_t vs. t (Fig. 8) give a straight line and the values of pseudo-second order constants can be obtained.

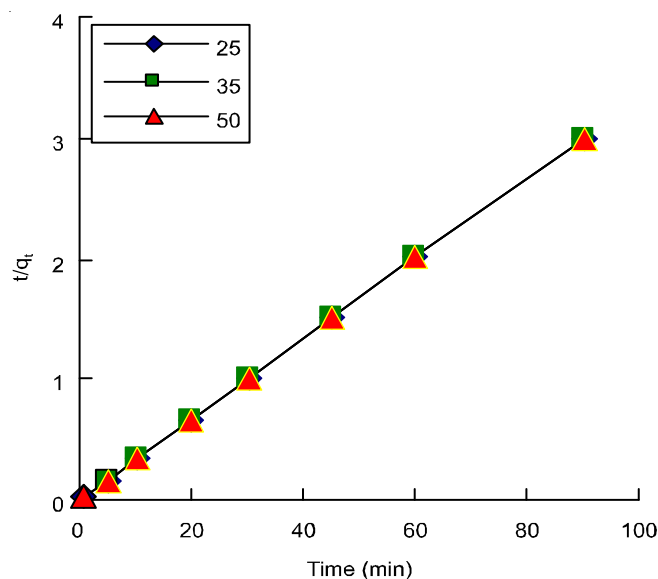


Fig. 8. Applicability of pseudo-second order kinetic model to dye adsorption

The kinetic parameters for adsorption of dye on base of palm leaf at different temperatures are shown in Table-2. The results show that the correlation coefficients of pseudo-second order model are greater than that of first order model. In addition, the calculated q_e values obtained from this kinetic model agree very well with the experimental q_e values. This finding suggested that adsorption of azure B on base of palm leaf surface follows second order kinetic model and the intraparticle diffusion may be the rate-controlling step.

In order to investigate the rate-limiting steps of adsorption process, the experimental data was also analyzed by intraparticle diffusion kinetics model²⁴:

$$q_t = k_d t^{1/2} + C \quad (9)$$

where k_d ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intraparticle rate constant and C (mg/g) is a constant. The plot of q_t versus $t^{1/2}$ is shown in Fig. 9 and the values of k_d , C and r^2 are 0.018, 29.789 and 0.865, respectively. The deviation of the straight line from origin point, indicates that intraparticle diffusion may not be the controlling step in the adsorption process of dye. The larger value of constant C (29.7), suggesting the greater effect of boundary layer²⁵.

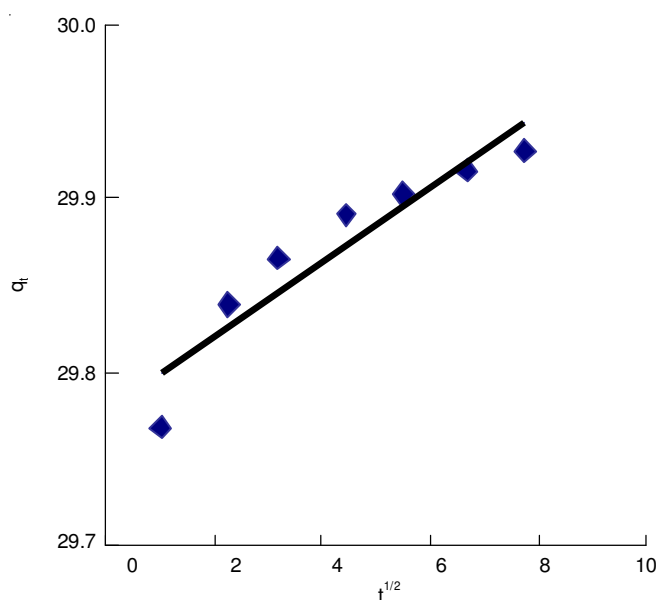


Fig. 9. Applicability of intraparticle diffusion kinetic model to dye adsorption at 25 °C

The activation energy of adsorption process was determined using Arrhenius equation²⁶:

$$\ln k_2 = \ln A - E_a/RT \quad (10)$$

where k_2 is the rate constant (g/mg min.), A is Arrhenius's factor (g/mg min), E_a is the activation energy (kJ/mol), R is the gas constant (J/mol K). Value of E_a was obtained from the slop of $\ln k_2$ versus $1/T$ (Fig. 10). The value of activation energy for

adsorption of azure B dye by base of palm leaf was reported to be 46.36 kJ/mol . This value reveals the possibility of chemisorption mechanism involved in the removal of dye by adsorbent surface²⁶.

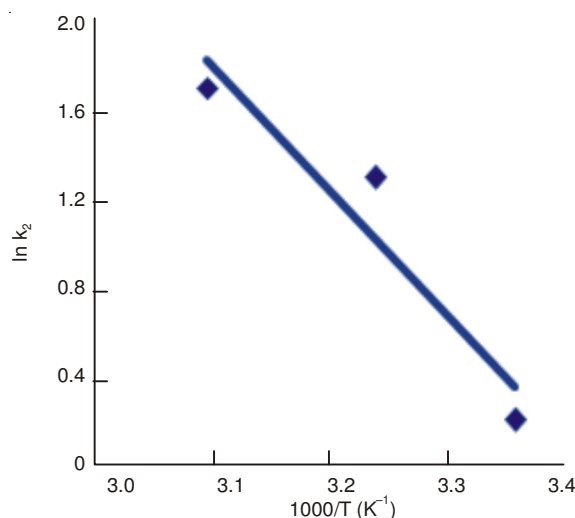


Fig. 10. Arrhenius plot for adsorption of azure B dye on base of palm leaf

Desorption studies: The desorption process was studied with different concentrations of dye. The results showed that an increase of dye concentration, increased the removal of dye from surface (Fig. 11). This may reflect a relatively high interaction between the dye and surface of adsorbent. The little amounts of dye removed from the surface, suggest the interaction of dye molecules with the surface may be specific and strong.

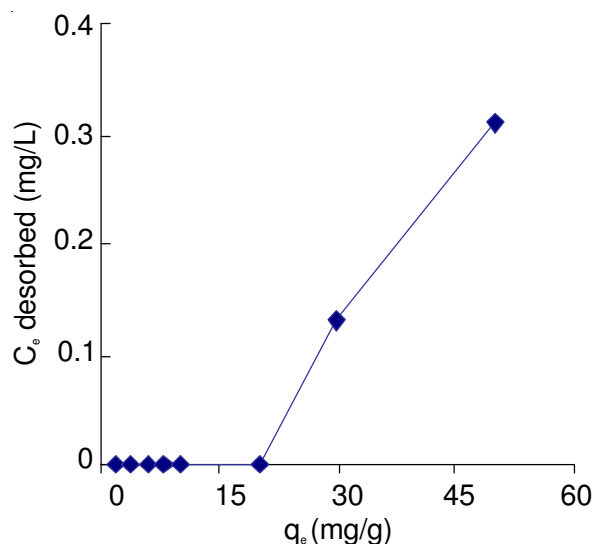


Fig. 11. Desorption of dye from base of palm leaf as a function of amount adsorbed at 25 °C

TABLE-2
KINETIC PARAMETERS FOR ADSORPTION OF AZURE B DYE ON BASE OF PALM LEAF AT DIFFERENT TEMPERATURES

T (K)	Pseudo-first order			Pseudo-second order			
	k_1 (min^{-1})	q_e (mg/g)	r^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg/g)	$h \times 10^3$ ($\text{mg g}^{-1} \text{min}^{-1}$)	r^2
298	0.041	0.144	0.972	1.239	29.940	1.111	1.000
308	0.075	0.114	0.836	3.718	29.940	3.333	1.000
323	0.094	0.120	0.843	5.577	29.940	5.000	1.000

Conclusion

Base of palm leaf surface appeared of high capacity for the removal of azure B dye from solution. The adsorption process of dye follows Langmuir model and the thermodynamic calculations show that the removal of dye by base of palm leaf was exothermic and spontaneous. Pseudo second-order kinetics model adequately described the adsorption process of dye at all temperatures, the intraparticle diffusion kinetics model indicates that intraparticle diffusion was not only rate controlling step in the adsorption process. The calculated value of activation energy reveals that adsorption of dye may take place through a chemical adsorption. Desorption studies shows that adsorption of azure B is strong with high affinity of dye molecules to surface of base of palm leaf.

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