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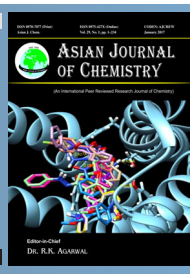

Adsorption of Amido Black 10B from Aqueous Solution Using Weed Waste as Adsorbent: Characterization, Equilibrium, Kinetic and Thermodynamic Studies

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In the present work, *Calotropis procera* leaf powder has been studied to assess its capacity for the adsorption of hazardous dye Amido black 10B from aqueous solution. The adsorbent has been characterized by scanning electron microscopy and Fourier transformer infrared spectrometer. The influence of various experimental parameters such as contact time, initial dye concentrations, adsorbent dosage, ionic strength, temperature and pH of dye solution has been studied. The adsorption process represented with Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherms. The maximum adsorption capacity of Amido black 10B onto adsorbent was 19.31 mg g^{-1}. Pseudo second order kinetics has been best fitted, with high correlation coefficients. The calculated values of thermodynamic parameters such as $\Delta H°$ and $\Delta S°$ for uptake of dye have been found to be 26.8811 kJ mol^{-1} and 78.5697 J mol^{-1} K^{-1}, respectively.

Keywords: Water remediation, *Calotropis procera*, Amido black 10B, Characterization, Environment.

INTRODUCTION

Dyes have been introduced into the natural water resources from different sources *e.g.*, pharmaceutical, textile industries, paper, pulp industries, dye and dye intermediates industries and Kraft bleaching industries which directly disturb the eco-system [1,2]. Amido black 10B (4-amino-5-hydroxy-3-[(4-nitrophenyl)azo]-6-(phenylazo)-2,7-naphthalene disulfonic acid, disodium salt) is an amino acid staining diazo dye, applicable to all kind of natural fibres like wool, cotton, silk as well as to synthetic fibres like polyesters, rayon and acrylic and also used in paints, inks, plastics and leather industries. It is highly toxic and damages the respiratory system of humans and is responsible for skin and eye irritations [3]. Hence, its removal from wastewater is an important issue from the environmental point of view. Comparatively few methods have been reported for the removal of toxic dye Amido black 10B [3,4]. In this respect, the adsorption has been found to be the most efficient process in this context for the removal of dyes and other pollutants from wastewater [5-8]. The cost of the adsorption process greatly depends upon the reuse of adsorbent and environment protection. *Calotropis procera* a wild growing plant of family 'Asclepiadaceae', is well known for its medicinal properties. The dried leaves were used as an expectorant and anti-inflammatory, for the treatment of paralysis, ulcers and rheumatic pains [9]. It is grown in most parts of the world in dry, sandy, alkaline soils and warm climate and is more common in south western and central India and western Himalayas. The aim of present study is to investigate the potential of *Calotropis procera* leaf powder as a novel low-cost adsorbent for the removal of Amido black 10B dye from aqueous solution.

EXPERIMENTAL

Adsorbent: The leaves of *Calotropis procera* have been naturally collected from Patiala city. The leaves have been washed five times with tap water to remove dirt particles from its surface. The biomass has been dried at 80 °C for 36 h, crushed in grinder and sieved through micron sized mesh. The dried powder of adsorbent has been preserved and characterized by using FTIR and SEM techniques.

Adsorbate: Amido black 10B is an amino acid staining diazo dye with molecular formula $C_{22}H_{14}N_6Na_2O_9S_2$ (CAS No. 1064-48-8, m.w. 616.49 g mol^{-1}, purity) has been used as procured. The stock solution of 1000 mg L^{-1} of dye has been prepared in deionized water.

Batch experimental procedure: The batch adsorption studies have been conducted to study the effect of different parameters such as; contact time, adsorbent dose, initial adsorbate concentration, pH and temperature. 100 mL solution of dye with initial concentration (10 to 60 mg L^{-1}) has been agitated along with fixed amount of adsorbent (0.1 to 1.1 g) on rotary orbital shaker at 120 rpm at 308.15 K until the

equilibrium has been established. The solution has been withdrawn at preset intervals of time and was filtered with the help of Whatman filter paper. The concentration of filterate has been measured with the help of Shimadzu-1800, UV-visible spectrophotometer at the maximum wavelength 618 nm. pH of the solution of dye has been adjusted with 1 N HCl and 1 N NaOH solutions. The amount of dye adsorbed and percentage removal of Amido black 10B have been calculated using eqns. 1 and 2, respectively:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

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

where C_0 and C_e are the initial and equilibrium concentrations of dye in solution (mg L^{-1}), V is the volume of the solution (L) and W is the mass of dry adsorbent (g).

RESULTS AND DISCUSSION

Characterization of adsorbent: SEM micrographs of adsorbent unloaded and loaded with Amido black 10B have been recorded and are shown in Fig. 1a and 1b. The images show a view from external side of adsorbent before and after the adsorption of dye. In the SEM micrograph 1a, the spots show the rough and porous surface of the adsorbent, which is responsible for increasing adsorption efficiency of the adsorbent. The dye loaded SEM micrograph shows that after adsorption the pores and surfaces of adsorbent were covered by dye (Fig. 1b).

The FTIR spectrum of Amido black 10B showed peaks at 3431, 2924, 1572, 1454, 1331, 1225 and 1047 cm^{-1} attributed to N–H stretching vibrations of aromatic primary amine, O–H stretching vibrations, N=N stretching vibrations, C–H bending vibrations, C–N bending vibrations, C–N stretching vibrations and S=O stretching vibrations of sulfonic acid respectively, while FTIR spectra of unloaded adsorbent consist of peaks at 2926, 1644, 1424, 1324, 1245, 1154 and 896 cm^{-1}, which may be attributed to asymmetric C-H bonds in alkyl groups, OH bending vibrations, C-O stretching, C-O groups on the biomass surface, C-F stretch due to strong alkyl halide, antisymmetric bridge C-OR-C stretching (cellulose), out of phase ring stretching [6,10] respectively. FTIR spectra of loaded adsorbent (Fig. 2) consist of peaks due to both dye and adsorbent but at shifted position. Thereby indicate the case of physiosorption.

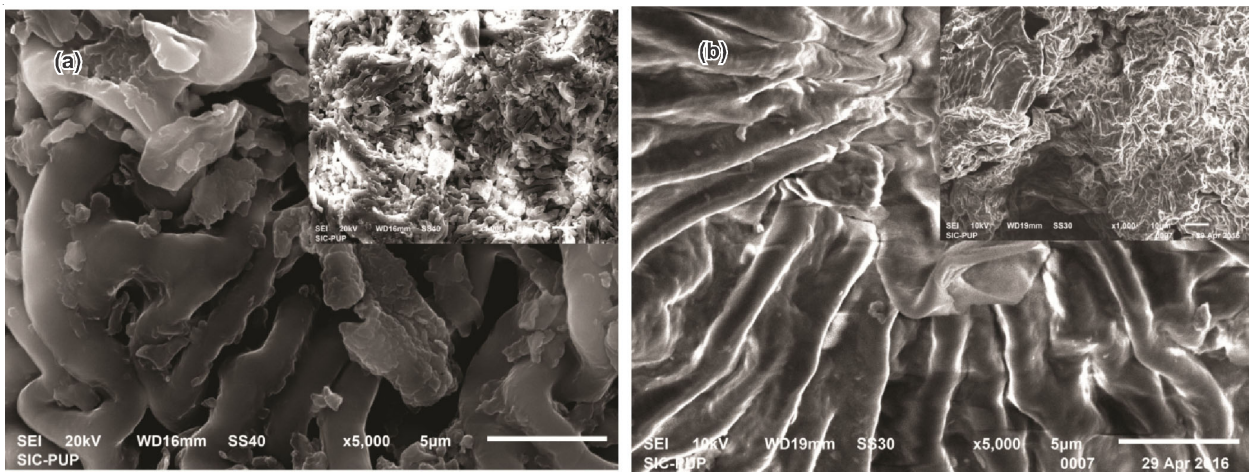

Fig. 1. SEM images of (a) adsorbent, (b) dye adsorbed onto adsorbent after Amido black 10B adsorption process

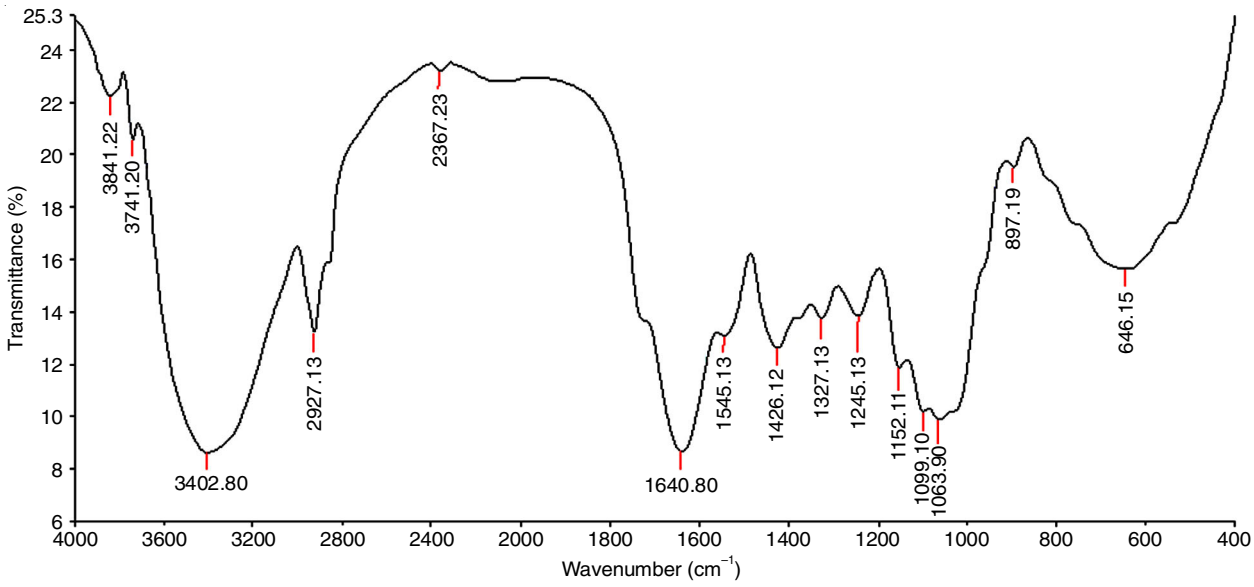

Fig. 2. FTIR spectra after adsorption of Amido black 10B

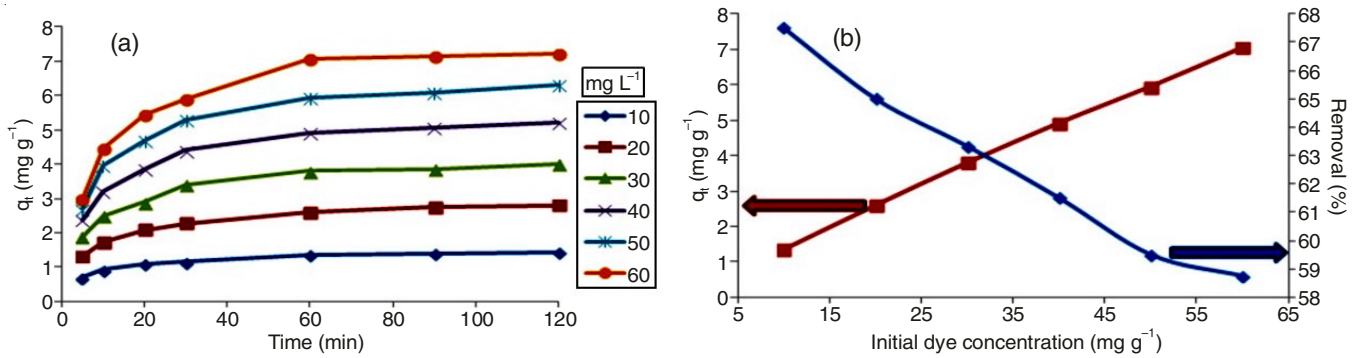

Fig. 3. Effect of (a) adsorption capacity (mg g^{-1}) as a function of contact time at different initial Amido black 10B concentrations, (b) percentage removal and adsorption capacity (mg g^{-1}) of Amido black 10B

Effect of contact time and initial dye concentrations: The equilibrium adsorption time for adsorption of dye on adsorbent has been determined by agitating the dye solution of initial concentration 10 to 60 mg L^{-1} along with 0.5 g of adsorbent at room temperature. The result of variation of adsorption capacity (amount adsorbed per unit mass) as a function of contact time (Fig. 3a) shows that dye uptake was initially rapid and then proceed at slower rate until it reaches a plateau, *i.e.*, after 60 min, equilibrium is established. At equilibrium, adsorption increases from 1.35 to 7.05 mg g^{-1}, with increase in initial dye concentration from 10 to 60 mg L^{-1} because of fact that initially there is rapid adsorption due to availability of large number of vacant sites and with passage of time, there is an accumulation of dye particles in the vacant sites leading to decrease in adsorption rate at the later stages [7]. Percentage removal of dye decreases from 67.50 to 58.75 % at concentration ranges from 10 to 60 mg L^{-1} (Fig. 3b), due to reason that at lower concentration the ratio of initial number of dye molecules to available surface is low and at higher concentration the ratio of number of dye molecules to available surface become high [10].

Effect of adsorbent dose: The effect of adsorbent dose on the removal of Amido black 10B has been investigated at a fixed initial dye concentration of 30 mg L^{-1} by increasing the adsorbent dosage from 0.1 to 1.1 g. The percentage removal increases from 8.33 to 88.33 %, whereas the adsorption capacity decreases from 5.00 to 2.41 mg g^{-1} (Fig. 4). Increase in adsorption efficiency with adsorbent dose may be attributed to increased surface area and the availability of more adsorption sites [1]. However, the adsorption capacity decreases with increase in dose as there may be unsaturated active sites on the adsorbent surface [11].

Effect of pH: It is evident from Fig. 5 that the process of adsorption is highly dependent on the pH of solution. The removal efficiencies of Amido black 10B decrease, with increase of pH. The maximum dye removal has been observed at pH 2.0 and thereafter the removal decreases. As at low pH, surface of adsorbent acquire positive charge and the presence of -SO_3 group is responsible for electrostatic attraction between positively charged surface and dye [12].

Effect of ionic strength: The effect of ionic strength of NaCl for the adsorption of Amido black 10B has been studied by varying the ionic strength from 0.001 to 0.1 mol L^{-1}. It is evident from Fig. 6 that with increase in ionic strength, adsorption of dye increases due to increase of electrostatic attraction between the positive charged surface of adsorbent and negatively charged dye [13].

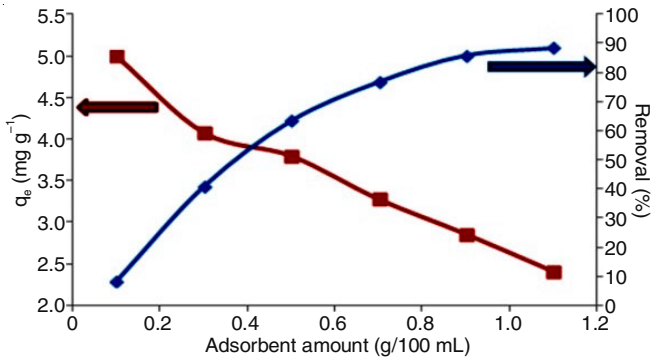

Fig. 4. Effect of adsorbent dose on removal dye

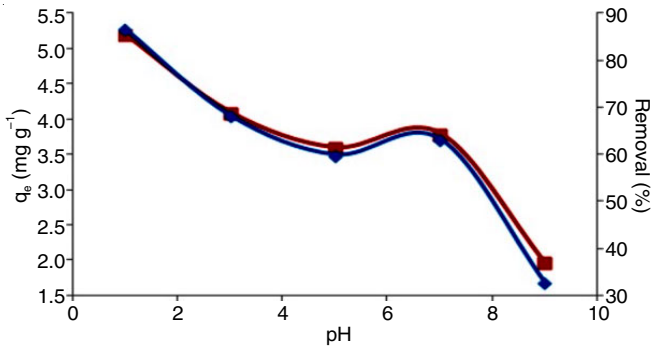

Fig. 5. Effect of pH on removal dye

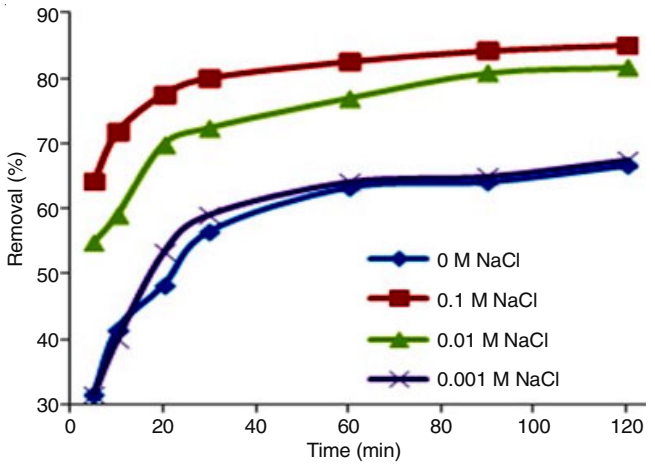

Fig. 6. Effect of ionic strength on the adsorption

Adsorption kinetics: Pseudo first order rate expression of Lagergren [14] is generally expressed by the following equation:

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303 \quad (3)$$

where, q_e and q_t are the amount of dye adsorbed at equilibrium (mg g^{-1}) at any time t (mg g^{-1}) respectively. But the data does not fit to straight line equation.

The pseudo second order rate [15] is expressed by follo-wing expression:

$$t / q_t = 1 / (k_2 q_e^2) + t / q_e \quad (4)$$

The plot between t/q_t and t gives a linear relationship (Fig. 7) with high coefficients (Table-1) *i.e.*, adsorption process follows pseudo second order kinetics.

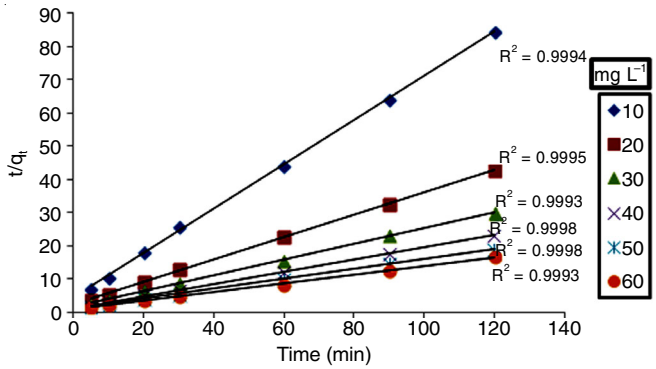

Fig. 7. Pseudo second order plot for Amido black 10B adsorption

Weber and Morris suggested [16] the following kinetic model to investigate whether the adsorption is intra-particle diffusion or not.

$$q_t = k_{ipd} t^{1/2} + C \quad (5)$$

where, k_{ipd} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and C is the constant (mg g^{-1}), which gives the thickness of the boundary layer. The intra-particle diffusion rate constant k_{ipd} and C are calculated from the slope and intercept of the plot q_t *versus* $t^{1/2}$ (Fig. 8) and the values along with their regression coefficient are listed in Table-1. According to this model, the linear portion of the plot does not pass through origin. It may

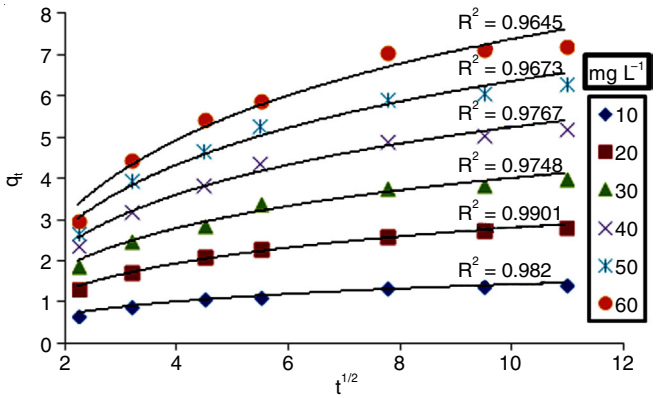

Fig. 8. Intra-particle diffusion study plot for Amido black 10B adsorption

be due to the variation of mass transfer in the initial and final stages of the adsorption process.

Adsorption isotherms: The linear form of Langmuir isotherm [17] is represented by the following equation:

$$C_e / q_e = C_e / q_m + 1 / q_m b_L \quad (6)$$

where, C_e is the equilibrium dye concentration in solution (mg L^{-1}), q_e is the dye concentration at equilibrium onto the adsorbent (mg g^{-1}), q_m is the dye concentration when monolayer forms on the adsorbent (mg g^{-1}) and b_L is the Langmuir constant related to the affinity of the binding sites and energy of biosorp-tion (L mg^{-1}). The value of b_L and q_m have been calculated from the intercept and slope of the plots C_e/q_e *versus* C_e and are given in Table-2.

To identify the feasibility and favourability of the adsorp-tion process a dimensionless constant separation factor (R_L) has been adopted. The separation factor (R_L) [18] is expressed by equation:

$$R_L = 1 / (1 + b_L C_0) \quad (7)$$

where, C_0 is the initial dye concentration (mg L^{-1}). The value of R_L indicates the type of isotherm, *i.e.*, favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). The value of R_L less than unity for this study and are contained in Table-2, states highly favourable adsorption for the adsorbate and adsorbent system.

TABLE-1
KINETIC PARAMETERS OF REACTION-BASED AND DIFFUSION-BASED MODELS FOR THE ADSORPTION OF AMIDO BLACK 10B ONTO ADSORBENT AT VARIOUS INITIAL DYE CONCENTRATIONS

Models	Parameters	10 mg L^{-1}	20 mg L^{-1}	30 mg L^{-1}	40 mg L^{-1}	50 mg L^{-1}	60 mg L^{-1}
Pseudo second order	k_2 (g mg^{-1} min^{-1})	0.0959	0.0434	0.0328	0.0245	0.0198	0.0164
	q_e (mg g^{-1})	1.5013	2.9718	4.2141	5.5067	6.6711	7.7339
	R^2	0.9994	0.9995	0.9993	0.9998	0.9998	0.9993
Intra-particle diffusion	k_{ipd} (mg g^{-1} $min^{-1/2}$)	0.0776	0.1612	0.2260	0.3019	0.3716	0.4482
	C (mg g^{-1})	0.6661	1.2205	1.7870	2.2691	2.6889	2.9533
	R^2	0.9820	0.9901	0.9748	0.9767	0.9673	0.9645

TABLE-2
ISOTHERM CONSTANTS FOR THE ADSORPTION OF AMIDO BLACK 10B ONTO ADSORBENT AT VARIOUS INITIAL DYE CONCENTRATIONS

Isotherm	Isotherm constants			
Langmuir	q_m (mg g^{-1}): 19.3050	b_L (L mg^{-1}): 0.0225	R_L: 0.4255-0.8163	R^2: 0.9840
Freundlich	n: 1.2337	K_F (mg g^{-1}): 0.2315	–	R^2: 0.9989
Tempkin	α (L g^{-1}): 0.1377	β (mg L^{-1}): 2.7579	b (J mg^{-1}): 928.9529	R^2: 0.9572
Dubinin-Raduske	q_D (mg g^{-1}): 5.3655	B (mol^2 J^{-2}): 1.5×10^{-6}	E (J mol^{-1}): 0.0017	R^2: 0.8444

Freundlich isotherm for heterogeneous surface system is represented as follows [19]:

$$\ln q_e = \ln K_F + (1/n)\ln C_e \quad (8)$$

where K_F (mg g^{-1}) and 1/n are the Freundlich constants, which are related to the adsorption capacity and the adsorption intensity of the system and determined from intercept and slope of plot of ln q_e *versus* ln C_e are given in Table-2.

Tempkin isotherm was considered the effects of indirect adsobate-adsorbent interactions and assumes that the heat of adsorption of all molecules on the layer should decrease linearly with the coverage [20]. The linear form of Tempkin relationship is given by:

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (9)$$

where, $\beta = (RT)/b$

Values of α and β are given in Table-2.

Dubinin-Raduskevich (D-R) isotherm is generally applied to express the adsorption mechanism with mean free energy distribution onto a heterogeneous surface [21].

$$\ln q_e = \ln q_D - B\varepsilon^2 \quad (10)$$

where B is a constant related to the mean free energy of adsorption (mol^2 J^{-2}), q_D is the theoretical saturation capacity (mg g^{-1}) and e is the Polyani potential which is calculated from the following equation:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (11)$$

The value of B and q_D were calculated from the intercept and slope of the plots ln q_e *versus* ε^2. The mean free energy E of adsorption per molecule of adsorbate has been calculated from equation:

$$E = 1/(2B^{0.5}) \quad (12)$$

Adsorption thermodynamics: The effect of temperature on adsorption gives important information about the nature of process. The adsorption process is studied at three different temperatures (298.15, 308.15, 318.15 and 328.15 K). It has been observed that the adsorption capacity increases with rise in temperature, *i.e.*, the process is endothermic in nature. Thermodynamic parameters such as change in the standard free energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$) have been determined [22] by using following equations:

$$\Delta G° = -2.303RT \log K_D \quad (13)$$

$$K_D = q_e/C_e \quad (14)$$

Also,
$$\Delta G° = \Delta H° - T\Delta S° \quad (15)$$

$$\ln K_D = \Delta S°/R - \Delta H°/RT \quad (16)$$

The values of $\Delta H°$ and $\Delta S°$ have been calculated from the slope and intercept of the plot of ln K_D *versus* 1/T (Fig. 9) and listed in Table-3. The low positive value of $\Delta H°$ (26.8811 kJ mol^{-1}) for *Calotropis procera* suggests that adsorption process is a physical in nature. The negative values of $\Delta G°$ indicate the feasibility of the system process [13]. The positive $\Delta S°$ (78.5697 J mol^{-1} K^{-1}) reflects the increase in randomness at the adsorbate at the solid-liquid interface which occurs due to desorption of water molecules from adsorbent surface during the process of adsorption.

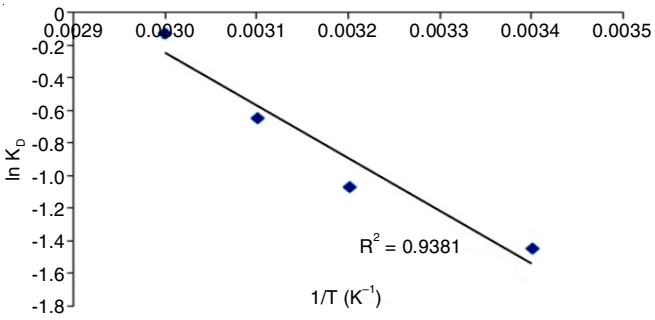

Fig. 9. Enthalpy and entropy determination for removal of dye

TABLE-3
THERMODYNAMIC PARAMETERS FOR AMIDO BLACK 10B ONTO ADSORBENT

Temp. (K)	K_D	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1}K^{-1})
298.15	1.1819	-0.4142	26.8779	91.9403
308.15	1.7273	-1.4003		
318.15	2.6364	-2.5641		
328.15	4.4546	-4.0757		

Desorption study: The results of desorption study has been shown in Fig. 10. The high adsorption percentage onto adsorbent has been found 80 % at optimized conditions in 1 % CH_3COOH as compare to HCl and NaOH. Thus the regenerated adsorbent has been reused for 5 times adsorption-desorption medium. The maximum desorption in acetic acid confirmed that the adsorption is mainly controlled by electrostatic attraction [23]. Thus it can be used as a potential adsorbent for the waste-water treatment.

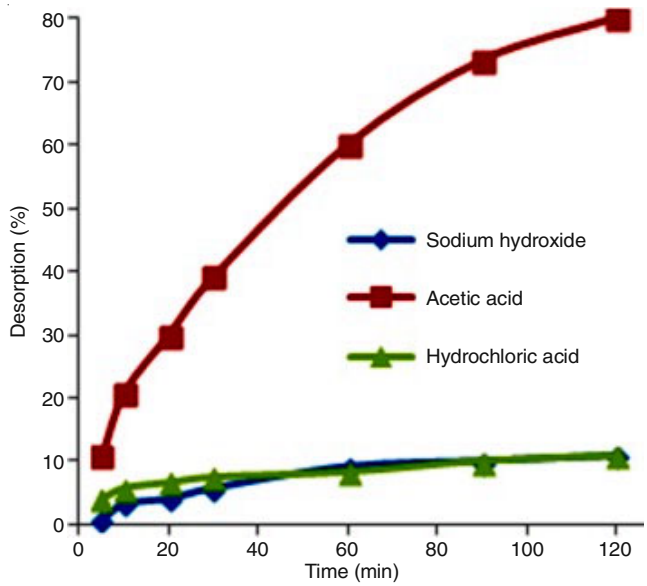

Fig. 10. Desorption studies of Amido black 10B

Conclusion

The present work is an effort to explore the use of adsorption method for the removal of toxic dye, Amido black 10B from aqueous solution using *Calotropis procera* leaf powder as an adsorbent (without giving any pretreatment). Equilibrium data have been fitted well in the Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm

models. The rate of adsorption has been found to be obeying pseudo second order kinetics, which is further followed by intra-particle with good correlation coefficients. The positive values of thermodynamic parameter standard enthalpy confirmed the endothermic nature of adsorption process.

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