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Adsorptive Removal of Amido Black 10B from Aqueous Solution using Stem Carbon of *Ricinus communis* as Adsorbent

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In the present work the efficiency of activated carbon made from stems of *Ricinus communis* (CRC) has been studied for removal of anionic dye- Amido black 10B from aqueous solution. The adsorbent has been characterized with scanning electron microscopy (SEM) and Fourier transformer infrared (FT-IR). The effects of various experimental parameters such as contact time, adsorbent dose, initial dye concentrations, pH, concentration of salt and temperature have been studied. Langmuir, Freundlich and Tempkin isotherm models have been used for describing the adsorption process. Of these, Langmuir isotherm model has best fitted the experimental data with a maximum adsorption capacity of 7.12 mg/g. Kinetics studies indicate that the adsorption of Amido black 10B has favoured toward pseudo-second-order model with high correlation coefficients. Thermodynamics parameters confirmed that the adsorption has been found to be spontaneous and endothermic in nature. These results suggested that CRC has a potential low-cost adsorbent for the removal of toxic dye Amido black 10B.

Keywords: Amido black 10B, Isotherm, Kinetics, *Ricinus communis*, Thermodynamics.

INTRODUCTION

Water pollution from synthetic dyes are commonly found in places, where textile industries are blooming. In dye process, azo colourants constitute an important class of synthetic coloured organic compounds (60-70 %), which are characterized by the presence of one or more azo bonds (R_1-N=N-R_2) [1]. Azo group dyes are toxic and carcinogenic which are not only created environmental and aesthetic problems, but also posed a great potential toxic threat to ecological and human health [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 with widespread applications, including dyeing wool, cotton, silk as well as to synthetic fibres like polyesters, rayon and acrylic [3]. It is highly toxic and damages the respiratory system of humans and is responsible for skin and eye irritations [3-5]. Hence removal of dye from effluent is an important issue from health, hygiene and environmental protection point of view. A limited number of studies have been reported for the treatment of toxic dye amido black 10B [3-5]. In this context, adsorption has got highest priority in terms of initial cost, ease of operation and simplicity of design [6-8]. The castor oil plant, *Ricinus communis* of the family 'Eurphorbiaceae' has not only medicinal properties but it also has great promises in the field of biodiesel production. Stems of this plant have been reported to exhibit anticancer, antidiabetic and antiprotozoal activities [8]. It has been used as an internal medicine for disorders like severe constipation, worm infestation, rheumatism, intestinal inflammation and also for facial paralysis, sore throat, furuncles, inflammation of the skin and ulcers [9]. It is indigenous in the most parts of the world and is more common in India, South Africa, China, Brazil and Russia [9]. In the present study stem carbon of *Ricinus communis* (CRC) has been explored as novel adsorbent, because it is renewable resource, biodegradable and eco-friendly, for the removal of amido black 10B from aqueous solution.

EXPERIMENTAL

Amido black 10B is an amino acid staining diazo dye (CAS No. 1064-48-8, m.w. 616.49 g mol^{-1}, λ_{max} 618 nm, purity) has

been obtained from SD Fine-Chem limited, Mumbai. All other chemicals such as; sodium hydroxide (NaOH), hydrochloric acid and sodium chloride, used in this work were of analytical grade. The stock solution of amido black 10B (1000 mg/L) has been prepared in deionized water and stored in a dark place to prevent direct contact with sun-light. All dilutions and washing have been carried out using deionized water.

Adsorbent: Adsorbent, *Ricinus communis* has been collected from Patiala city. The stems of adsorbent have been washed with tap water to remove dirt particles from its surface and then finally with deionized water. The washed biomaterial has been dried in an oven for five days and then it has carbonized. The carbonized sample has washed with hot deionized water and again dried at 80 °C for 24 h. The dried biomaterial has been smashed into fine powder and sieved through micron sized mesh. Carbonized adsorbent has been stored in airtight container for the subsequent use.

Batch adsorption procedure: Batch adsorption experiments have been carried out by taking 100 mL solution of dye with initial dye concentration (100 mg/L) with fixed amount of adsorbent (2.0 g). The mixtures have been agitated mechanically at 250 rpm and 298.15 K until the equilibrium reached. The adsorbent has been separated from the resultant mixture by filtration using Whatman filter paper and then centrifuged at 2000 rpm for 10 min. The equilibrium concentration of amido black 10B in solution has been measured at 618.00 nm with the help of UV-visible spectrophotometer (Shimadzu-1800). The experimental conditions have been optimized at contact time (10-80 min), initial dye concentrations (25-150 mg/L), adsorbent dosage (0.5-3.0 g), pH (1-9) and temperature (298.15-328.15 K). pH of solution has been adjusted with 0.1 N HCl or 0.1 N NaOH solutions. The amount of equilibrium adsorption, q_e (mg/g) and percentage removal of dye has been calculated [8] by using equations:

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

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

where, C_o is the initial concentration of the dye in solution (mg/L), C_t is the liquid-phase concentration of dye at any time (mg/L), V is the volume of the solution (L) and W is the mass of dry adsorbent (g).

RESULTS AND DISCUSSION

Characterization of CRC: The morphological characterization of the particle of CRC surface has been studied with a JEOL model JSM6610 scanning electron microscope (SEM) operated at 30 kV. It is clear from Fig. 1a that adsorbent has irregular and porous structure. Thus, there is a good possibility for amido black 10B to be diffused through pores. Fig. 1b shows that after adsorption of dye, the surface morphology of CRC has changed and the pores get packed.

Fourier transformer infrared (FT-IR) spectrum of amido black 10B, CRC and after dye adsorption has been recorded on a Perkin Elmer spectrophotometer-RZX using KBr pellets in the region of 4000-450 cm^{-1}. FT-IR spectrum of unloaded CRC before adsorption of dye (Fig. 2a) consist of the characteristic peaks [10] of calcite at 875 and 712 cm^{-1}. The other peaks appear at 3696, 2984, 1461 and 1054 cm^{-1}, which may be due to stretching vibrations of O–H group, C–H stretching, symmetric stretching vibrations of C=O and C–OR stretching of cellulose, respectively. FT-IR spectrum of dye-loaded CRC (Fig. 2b) consists of peaks due to both adsorbent and dye at slightly shifted positions. This shift in the absorption peaks suggested the interactions of amido black 10B dye molecules with adsorbent.

Effect of contact time and initial dye concentration on adsorption: The equilibrium adsorption time for adsorption of amido black 10B onto CRC has been studied over the range of initial dye concentrations (25-150 mg/L) along with 2.0 g of adsorbent at 298.15 K. The result of variation of adsorption capacity (amount adsorbed per unit mass) as a function of contact time has been fast initially and then proceed at slower rate until it reaches a plateau, *i.e.*, after 50 min (Fig. 3a), equilibrium is established. The initial fast rate of adsorption capacity may be explained by the fact that initially availability of large number of binding sites for adsorption. But with increase of contact time, there is an accumulation of dye particles in the

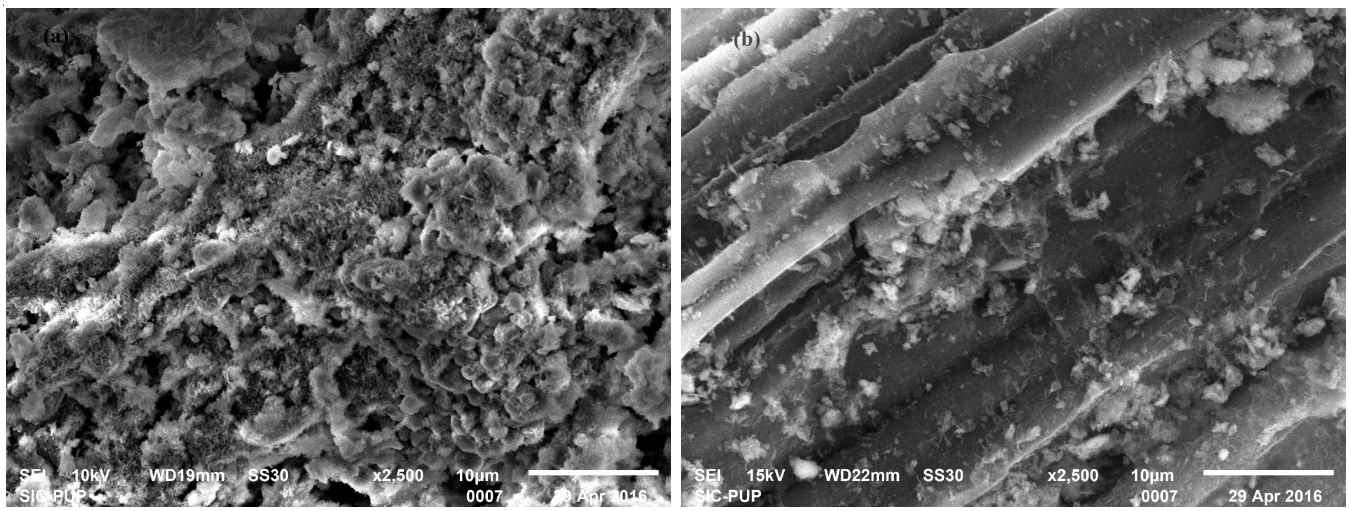

Fig. 1. SEM micrograph showing (a) CRC as adsorbent before adsorption, (b) CRC adsorbed with amido black 10B dye

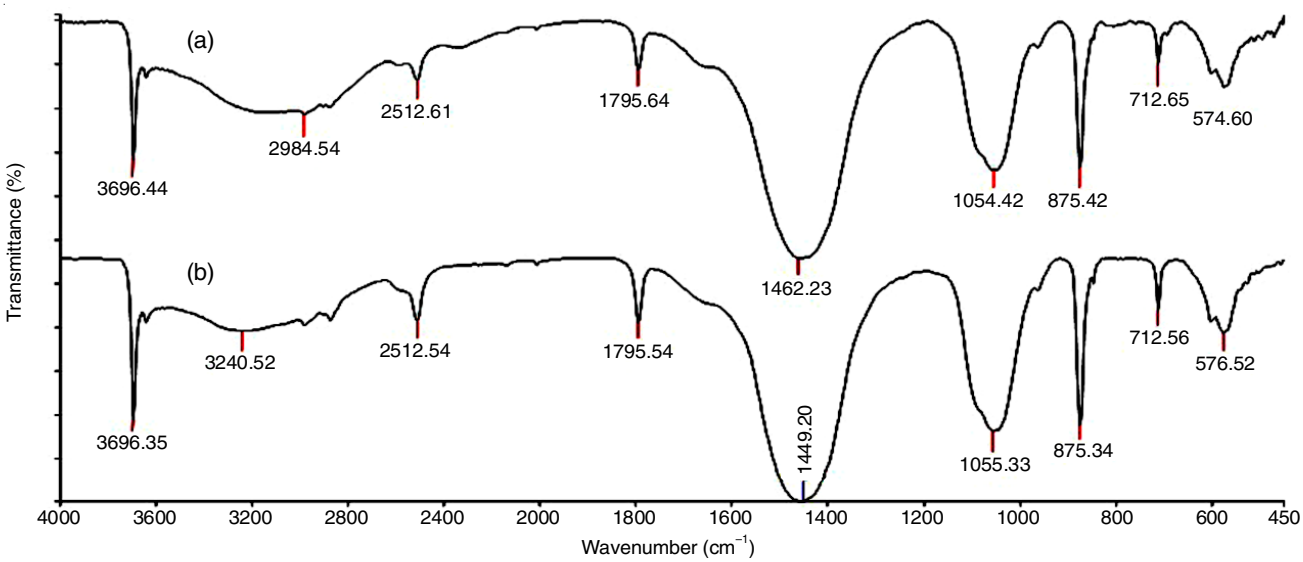

Fig. 2. FT-IR spectrum of (a) neat CRC, (b) after adsorption of amido black 10B on the surface of CRC

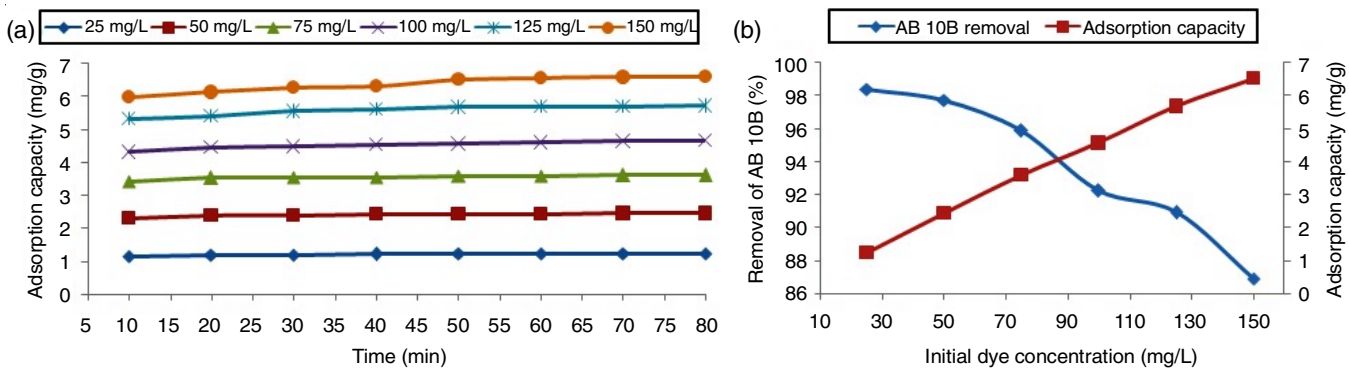

Fig. 3. (a) Effect of contact time on adsorption of amido black 10B onto CRC at different initial dye concentrations and (b) Effect of initial dye concentration on adsorption of amido black 10B using CRC

slower adsorption rate at the end is due to the saturation vacant sites leading to slower rate of adsorption at later stages [8].

The variation of dye removal and adsorption capacity as a function of initial dye concentration indicate (Fig. 3b) that percentage removal decreases from 98.40 to 86.93 % at concentration ranges from 25-150 mg/L. It may be due to that the adsorbent has a limited number of active sites, which does not allow further adsorption to take place. But with increase the initial dye concentration results in an increase in adsorption capacity onto CRC from 1.23 to 6.52 mg/g, because it provides a driving force to overcome all mass transfer resistances of dyes between solid phase and liquid phase.

Effect of adsorbent dose: In order to study the effect of adsorbent dose, batch experiments have been conducted at a fixed dye concentration of 100 mg/L by increasing the adsorbent dosage from 0.5 to 3.0 g. The percentage removal of dye increases from 54.00 to 98.00 %, whereas the adsorption capacity decreases from 10.80 to 3.27 mg/g for CRC dosage of 0.5 to 3.0 g respectively (Fig. 4). Increase in adsorption efficiency may be due to reason that the availability of more binding sites as the dose of adsorbent increases. However, the mass adsorbed per unit mass decreases with increase in dose of CRC as there may be unsaturated active sites on the surface of adsorbent [6].

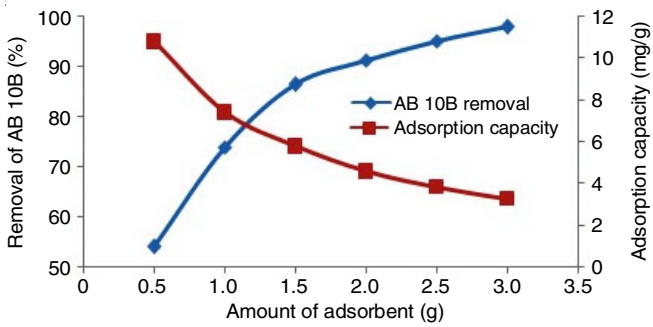

Fig. 4. Effect of amount of adsorbent on the adsorption of amido black 10B onto CRC

Effect of pH: The effect of pH on the adsorption of dye by CRC has been studied in between pH 1-9. The result has been obtained are shown in Fig. 5, which described the maximum adsorption at pH 1.0 and thereafter the adsorption deceases. At low pH, high electrostatic attraction exists between the positive charged surface of CRC and -SO_3 group of dye, which leading to the maximum removal of dye [11].

Effect of concentration of salt: The effluent from dyeing industries contains suspended and dissolved compounds, acids, alkalis, salts and metal ions. Due to the presence of these salts, ionic strength of the solution increased. The effect of ionic

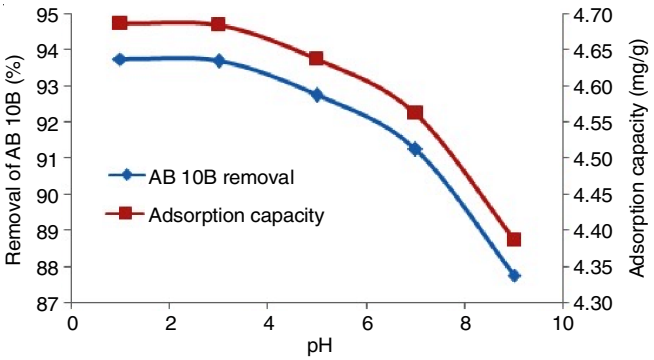

Fig. 5. Effect of pH on the adsorption of amido black 10B onto CRC

strength of NaCl for adsorption of dye has been investigated by varying the amount of NaCl from 0.001 to 0.1 mol/L. It is evident from Fig. 6 that the removal of dye increases due to increase of electrostatic attraction between surface of adsorbent and dye. The addition of NaCl increases the aggregation of dye molecules, which promotes the adsorption process.

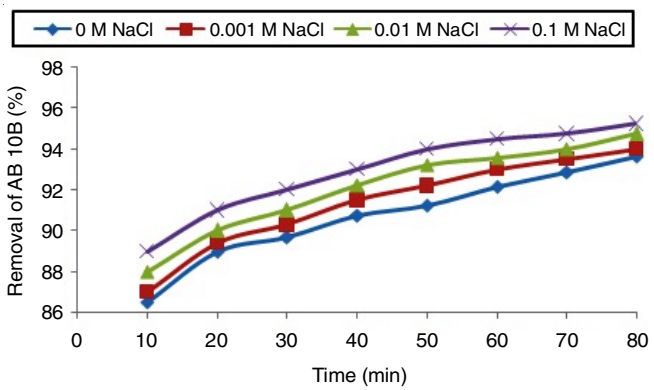

Fig. 6. Effect of concentration of salt on the adsorption of amido black 10B onto CRC

Langmuir isotherm model: Langmuir adsorption isotherm, assumes that adsorption takes place at specific homogenous sites within adsorbent and the linear form of Langmuir isotherm is [12]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_L} \quad (3)$$

where, C_e (mg L^{-1}) and q_e (mg g^{-1}) are the equilibrium dye concentration in solution and the adsorbent respectively; q_m (mg g^{-1}) and b_L (L mg^{-1}) are monolayer capacity and Langmuir constant related to the affinity of the binding sites and energy of biosorption. The value of b_L and q_m have been calculated from the intercept and slope (Table-1). The feasibility and favourability of the adsorption process are calculated by a dimensionless constant separation factor (R_L) and is expressed by the following equation:

$$R_L = \frac{1}{1 + b_L C_o} \quad (4)$$

The parameter values of R_L have been less than unity for this study and are contained in Table-1, states highly favourable adsorption for amido black 10B and CRC system.

It is interesting to note that a very few work [3,4,13,14] has been reported for the removal of anionic dye, amido black 10B due to its low rate of removal on adsorbents. Table-2 shows that the CCP used in this work has higher adsorption capacity (without any treatment) as compared to other few reported adsorbents for toxic dye amido black 10B.

TABLE-1
ISOTHERM CONSTANTS AND CORRELATION COEFFICIENTS FOR THE ADSORPTION OF AMIDO BLACK 10B ONTO CRC

Isotherm	Parameters	Values
Langmuir	q_m (mg/g)	7.1174
	b_L (L/mg)	0.3608
	R_L	0.0998-0.0181
	R^2	0.9761
Freundlich	n	2.4533
	KF [(mg/g)(L/mg)$^{1/n}$]	2.0435
	R^2	0.9704
Tempkin	α (L/mg)	5.6859
	β	1.3111
	b_T (J/mol)	1890.6407
	R^2	0.9732

TABLE-2
COMPARISON OF ADSORPTION CAPACITIES OF VARIOUS ADSORBENTS FOR THE ADSORPTION OF AMIDO BLACK 10B

Name of adsorbent	q_m (mg/g)	Ref.
Leaf powder of *Calotropis procera*	19.31	[4]
Hen feather	12.95	[3]
Orange peel	7.90	[13]
Banana peel	6.50	[13]
Clinoptilolite	0.01	[14]
CRC	7.12	Present study

Freundlich isotherm model: Freundlich adsorption isotherm is an empirical equation based on the adsorption onto a heterogeneous surface and the linear form of Freundlich equation is [15]:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (5)$$

where, K_F [(mg/g)(L/mg)$^{1/n}$] and n are the Freundlich constants, which are related to the adsorption capacity and the adsorption intensity of the system and are given in Table-1. The value of n (*i.e.*, > 1) indicates the favourable adsorption of dye with adsorbent.

Tempkin isotherm: Tempkin isotherm takes has been considered the effects of indirect adsobate-adsorbent interactions. The linear form of Tempkin [8] relationship is given as:

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (6)$$

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

where, T is the absolute temperature in Kelvin, R is the universal constant and b is the Tempkin constant related to heat of adsorption (J/mg). The value of Tempkin constants α and β are listed in Table-1.

Kinetics data: The integrated linear form of pseudo-first-order (eqn. 7), pseudo-second-order (eqn. 8) and Weber-Morris intra-particle diffusion (eqn. 9) are expressed as [16-18].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

TABLE-3
KINETIC PARAMETERS FOR THE ADSORPTION OF AMIDO BLACK 10B ONTO CRC

Models	Parameters	Amido black 10B (mg/L)					
		25	50	75	100	125	150
Pseudo-second-order	k_2 (g/mg min)	0.8527	0.5621	0.3609	0.1487	0.1408	0.0780
	q_e (mg/g)	1.2564	2.4813	3.6523	4.7348	5.8139	6.7521
	R^2	1.0000	1.0000	1.0000	0.9998	0.9999	0.9997
Intra-particle diffusion	k_{ipd} (mg/g $min^{1/2}$)	0.0121	0.0205	0.0308	0.0576	0.0727	0.1131
	C (mg/g)	1.1418	2.2915	3.3653	4.1650	5.1254	5.6490
	R^2	0.9216	0.8427	0.8661	0.9844	0.9370	0.9623

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

where k_1 (min^{-1}), k_2 (g/mg/min) and k_{ipd} (mg/g/$min^{-1/2}$) are the rate constants of adsorption for pseudo-first-order model, pseudo-second-order model and intra-particle diffusion respectively. C (mg/g) is the constant, which gives the thickness of the boundary layer. But the data confirmed the non-applicability of pseudo-first-order kinetic model. The kinetic parameters for adsorption of dye onto CRC using a fixed amount of adsorbent 2.0 g over the initial amido black 10B concentrations in the range of 25-150 mg/L at constant pH and temperature have been listed in Table-3. The linear plot of t/q_t *versus* t shows that the high correlation coefficients, which confirmed pseudo-second-order nature of the process (Fig. 7). The linearity of the plot q_t *versus* $t^{1/2}$ shows that the linear portion of the plot does not pass through origin and this deviation from the origin may be due to the variation of mass transfer of adsorption in the initial and final stages. This confirmed that adsorption of dye onto CRC has been a multi-step process [11].

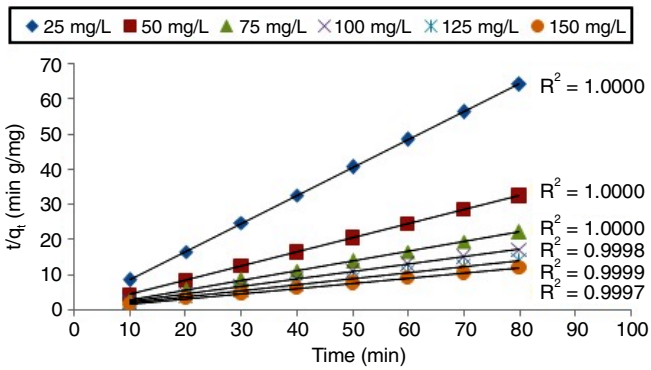

Fig. 7. Pseudo-second-order kinetic model

Thermodynamic study: Thermodynamic data for the adsorption of dye onto adsorbent provide information of the feasibility of process. The thermodynamic parameters, such as; change in free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) have been calculated for adsorption of amido black 10B onto CRC at different temperature (298.15, 308.15, 3318.15 and 328.15 K) from the following relation [4,11]:

$$\Delta G = -2.303RT \log K_D \quad (10)$$

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

$$\ln K_D = \Delta S/R - \Delta H/RT \quad (12)$$

$$K_D = q_e/C_e \quad (13)$$

where R (8.314 J/mol K) and K_D (K/g) are the universal gas constant and distribution coefficient for adsorption of dye. The thermodynamic values have been calculated from the slope and intercept of the plot of ln K_D *versus* 1/T and are summarized in Table-4. The positive value of ΔH (4.189 kJ/mol) for adsorption of dye suggested the endothermic process. The negative values of ΔG at different temperatures indicate the feasibility of the system. The positive entropy change ΔS value (33.625 J/mol/K) reflects the increase in randomness at the solid-solution interface [11].

TABLE-4
THERMODYNAMIC PARAMETERS FOR AMIDO BLACK 10B ONTO CRC

T (K)	ln K_D	-ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	R^2
298.15	2.3445	5.8115	4.1888	33.6251	0.9567
308.15	2.4088	6.1712			
318.15	2.4768	6.5513			
328.15	2.5489	6.9540			

Conclusion

On the bases of observed results, it has been concluded that carbon made from stem of *Ricinus communis* (without any chemically modification) act as potential adsorbent for the removal of hazardous amido black 10B from aqueous solution. The adsorbent is easily available, inexpensive and biodegradable. The equilibrium adsorption data have been described by Langmuir, Freundlich and Tempkin isotherms with a maximum monolayer adsorption capacity found to be 7.12 mg/g. The rate of adsorption has found to be obey pseudo-second-order kinetics with high values of correlation coefficient. The results of thermodynamic parameters inferred that adsorption of amido black 10B onto the adsorbent spontaneous and endothermic in nature.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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