Research Article

Adsorption of Congo red dye from aqueous solution onto Ash of *Cassia Fistula* seeds: Kinetic and Thermodynamic Studies

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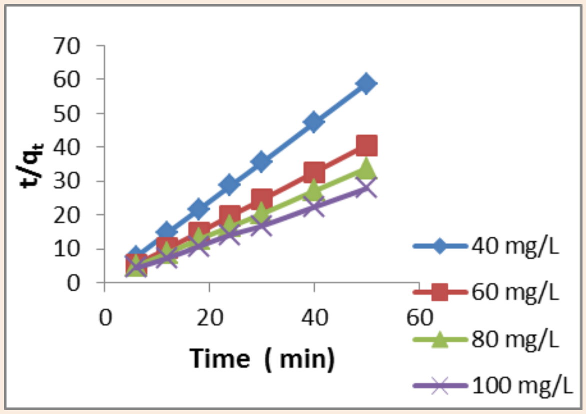
Abstract

This paper presents the feasibility of removal of anionic azo dye Congo red from aqueous solution onto ash of *Cassia fistula* seeds by using adsorption technique. Batch adsorption studies showed that adsorption of dye increased with increase in contact time and adsorbent dose. The equilibrium adsorption data have been analyzed by using Langmuir and Freundlich adsorption isotherms. The adsorption kinetic data were modeled using pseudo-first-order, pseudo-second-order and intra-particle-diffusion model. The kinetic adsorption data well fitted to pseudo-second order kinetic model and intra-particle-diffusion model. Thermodynamic parameters such as ΔG, ΔH and ΔS were calculated. The negative value of ΔG and ΔH indicates the spontaneous and exothermic nature of adsorption and there is decrease in entropy at solid-liquid interface. Dimensionless separation factor and heterogeneity factor showed that ash of *Cassia fistula* seeds can be used as an alternative to commercial adsorbents for the removal of Congo red from aqueous solution and effluents.



Keywords: Adsorption, Congo red dye, ash of *Cassia fistula* seeds, isotherms, kinetic

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Introduction

Water resources are of critical importance to both natural ecosystem and human development. But in recent years, there is a drastic increase in water pollution and the quality of water deteriorating day by day due to continuous discharge of various organic dyes used in the industries like textile, paper, food, cosmetics, etc. into water resources [1]. Today, there are over 1,00,000 dyes for the commercial use and around 7×10^5 tons of dye stuff are produced annually [2]. Congo red dye used in present investigation is an anionic azo dye and is known carcinogen causes blood clotting, respiratory problems and on ingestion, it produces gastrointestinal irritation with nausea, vomiting and diarrhea [3-4]. So, there is need to treat the wastewater containing this toxic dye before it's discharged into water bodies.

A number of treatment techniques reported in literature have been applied for the removal of dyes including electrocoagulation, biodegradation, electrochemical oxidation, membrane separation [5-8] etc. All these techniques have significant disadvantages such as handling and disposal problems and production of toxic sludge. Among all these numerous techniques adsorption has been considered as the best wastewater treatment method due to its high efficiency, low cost, easy availability of adsorbents, easy operation and ability to treat dyes in more concentrated form [9]. Various types of materials like activated carbon, fly ash, coal [10-12] etc. has been reported in literature for the removal of dyes. Among all these, activated carbon is most efficient, but its uses are limited due to its high cost [13]. So, low-cost biodegradable adsorbents such as rice husk, neem leaf and orange peel, cashew nut shell, miswak stems, cotton [14-18] etc. have received considerable attention as it offers the most economical and effective removals option. *Cassia fistula* is medicinally important plant and is wide spread [19]. Ash of *Cassia fistula* seeds has been used as adsorbent. So, the main objective of the present study is to explore the adsorption technique for the removal of Congo red dye by using ash of *Cassia fistula* seeds as low-cost adsorbent.

Materials and Methods

Adsorbent:

The fruit of *Cassia fistula* has been collected from University campus. The ripe seeds has been separated from the pods and washed with water to remove the pulp outside the seeds. The washed seeds then completely dried, burnt and crushed into powder form. The carbonized material obtained was washed with distilled water till the colour of washing becomes clear and then kept in the oven to dry completely. The dried ash was crushed into fine powder and sieved in uniform size particle.

Adsorbate:

Congo red dye is (Naphthalene sulfonic acid,3,3'–(4,4'-biphenylene bis (azo) bis (4–amino) disodium salt) has molecular formula $C_{32}H_{22}N_6Na_2O_6S_2$. Congo red dye (C.I.No. = 22120, C.A.S.No = 573-58-0) was purchased from S.D. Fine Chemical limited Mumbai, India. Stock solution of dye was prepared by dissolving 0.1 g of dye in 1000 mL of distilled water and the other concentrations have been prepared by successive dilution of stock solution.

Adsorption experiments:

In adsorption experiments, 100 mL of dye solution of definite concentrations containing definite amount of adsorbent (4.0 g) was agitated at 450 rpm with the help of mechanical shaker. The temperature was kept constant (308 K). 5 mL of solution has been withdrawn at preset intervals of time and then centrifuged. The amount of dye left in solution was analyzed by using UV-Visible Spectrophotometer from which amount of dye adsorbed has been calculated. The amount of dye adsorbed per gram of adsorbent, i.e., q_t at time t, has been calculated by the following formula

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

Where, C_t (mg/L) is the liquid-phase concentration of dye at any time t, C_o (mg/L) is the initial concentration of dye in solution; V is the volume of the solution (L) and W is the mass of adsorbent (g). The percentage of dye removed was calculated by the following formula:

$$\frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Result and Discussion

Effect of contact time:

In order to study the effect of contact time, 100 mL of dye solution (60 mg/L) has been agitated along with 4.0 g of adsorbent for different intervals of time (6, 12, 18, 24, 30, 40 and 50). The percentage of dye removed and adsorption capacity increased with increase in contact time (**Figure 1**). Both these factors increases with contact time and adsorption equilibrium has been attained within 30 minutes of agitation. At the initial stages, large numbers of surface sites are available for adsorption, but with increase of contact time, more and more dye particles get adsorbed on the surface and free surface for adsorption decreases. A comparison of contact time for the adsorption of Congo red dye onto ash of *Cassia fistula* seeds with other adsorbents (**Table 1**) shows that ash of *Cassia fistula* seeds takes lesser contact time for adsorption.

Table 1 Contact time for Congo red adsorption on various adsorbents

Adsorbent	Equilibrium Contact time	References
Marine alga *Porphyra yezoensis Ueda*	400 min	[20]
Marine algae *Valoria bryopsis*	180 min	[21]
Ash of *Cassia fistula* seeds	**30 min**	**Present study**

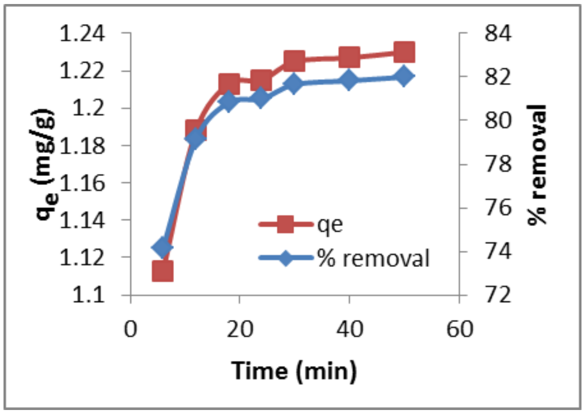

Figure 1 Effect of contact time (C_0 = 60 mg/L, adsorbent dose = 4.0 g, agitation speed = 30 min, T = 308 K)

Effect of initial dye concentration:

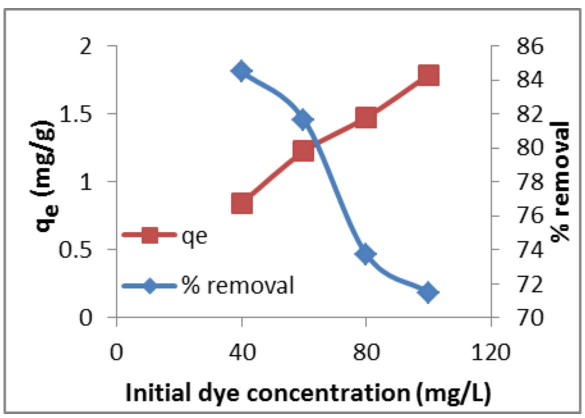

Figure 2 Effect of initial dye concentration (C_0 = 60 mg/L, adsorbent dose = 4.0 g, agitation speed = 30 min, T = 308 K)

4.0 g of ash of *Cassia fistula* seeds has been added to 100 mL solution of different initial dye concentrations (40, 60, 80 and 100 mg/L) and was agitated for 30 minutes (equilibrium time). Experiments have been conducted at constant temperature and pH. The result shows (**Figure 2**) that percentage removal of dye decreases with increase in dye concentration, as at higher concentration the available sites on the adsorbent becomes limited and there is no more adsorption. But adsorption capacity increase with increase in initial dye concentration, which is attributed to the fact that within increase of concentration of dye, all the sites of adsorbent get saturated, thus all the active sites get occupied and thereby result in increase of adsorption capacity.

Effect of adsorbent dosage:

Adsorbent dose is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of adsorbate. The removal of Congo red (60 mg/L) has been studied at different adsorbent dose (1.0, 2.0, 3.0, 4.0 and 5.0 g). The result (**Figure 3**) indicates that as adsorbent dose increase from 1.0 to 5.0 g, percentage removal increases from 47.50 to 84.00 % as with increase of adsorbent dose there is increase in surface area and hence number of adsorption sites available for adsorption but adsorption capacity decreases from 2.850 to 1.008 mg/g with increase in the adsorbent dose due to reason that adsorption sites remain unsaturated during the adsorption process.

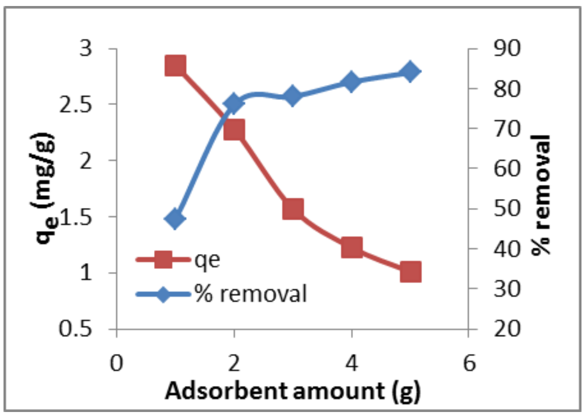

Figure 3 Effect of adsorbent dose (T = 308 K, C_0 = 60 mg/L, agitation time = 30 min)

Effect of pH:

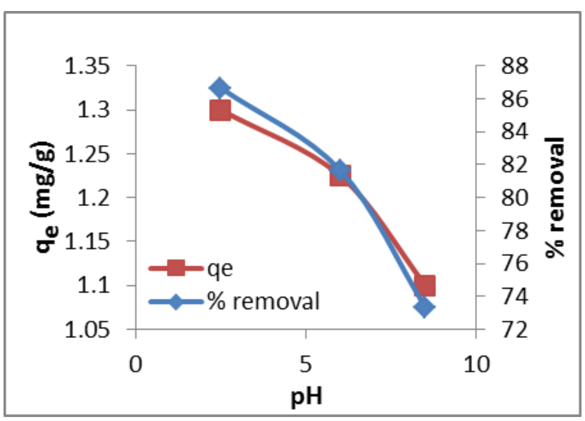

Figure 4 Effect of pH (adsorbent dose = 4.0 g, C_0 = 60 mg/L, T = 308 K)

In order to study the effect of pH, 100 mL dye solution (60 mg/L) and 4.0 g of adsorbent has been agitated at three different pH (2.5, 6.0 and 8.5). With increase of pH of dye solution, the percentage removal decrease from 86.66 to 73.33% and adsorption capacity decreases from 1.30 to 1.10 mg/g (**Figure 4**). The maximum removal of dye has been recorded at lower pH because low pH leads to an increase in H^+ ions concentration. So the surface of adsorbent acquires a positive charge by absorbing H^+ ions and there is significant strong electrostatic attraction appears between the positively charged adsorbent surface and anionic dye molecule, which leads to maximum adsorption. As the pH of system increases, number of positively charged sites decreases which leads to decrease of adsorption capacity and also decrease of percentage of dye removed.

Effect of temperature:

To observe the effect of temperature, adsorption studies of Congo red onto ash of *Cassia fistula* seeds were performed at three different temperatures: 308, 313 and 318 K. It has been observed (**Figure 5**) that both adsorption capacity and percentage of dye removed decreases with the rise of temperature. It may be attributed to the fact that either the increase in temperature leads to desorption or swelling effect of internal structure of adsorbent, which results in decrease of adsorption.

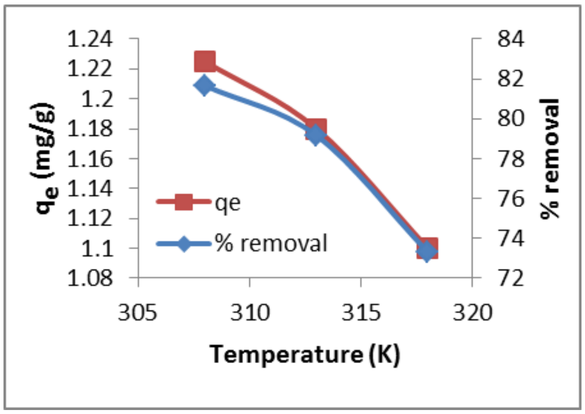

Figure 5 Effect of temperature (C_o = 60 mg/L, adsorbent dose = 4.0 g)

Adsorption isotherms:

Langmuir and Freundlich adsorption isotherms were selected for this study.

Langmuir isotherm:

A well-known linear form of the Langmuir equation can be expressed as:

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

Where, q_m and b_L are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg). The linear plot between C_e / q_e verses C_e (**Figure 6**) shows that adsorption follows Langmuir isotherm. The values of constants q_m and b_L have been evaluated from the slope and intercept of the plot and listed in **Table – 2**. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L, which is defined by equation:

$$R_L = \frac{1}{(1+b_L.C_0)}$$

The R_L value obtained is 0.1655 which lies between 0 and 1, thereby confirms that adsorption is favourable.

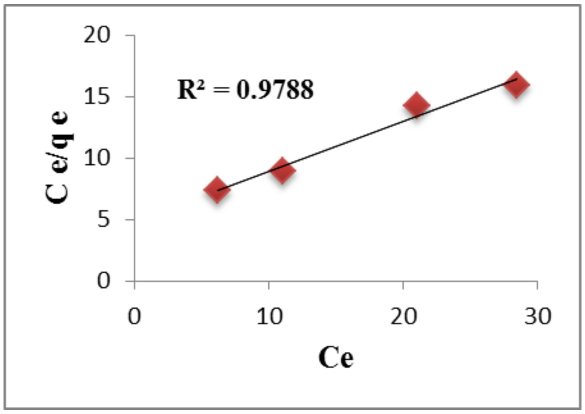

Figure 6 Langmuir adsorption isotherm for Congo red adsorption

Freundlich isotherm:

Freundlich isotherm can be described by the equation given below:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where, K_f is Freundlich constant and 1/n is the heterogeneity factor. The value of n and K_f has been calculated from the slope and intercept of plot between log q_e verses log C_e respectively (**Figure 7**) and are given in **Table 2**. The value of Freundlich constant n is greater than 1, which indicates favourable adsorption.

Table 2 Langmuir and Freundlich constants

Adsorption system	Langmuir constants			Freundlich constants		
	q_m (mg/g)	b_L (L/mg)	R^2	N	K_f	R^2
Congo red – ash of Cassia fistula seeds	2.46	0.0840	0.9788	2.1626	0.3766	0.9733

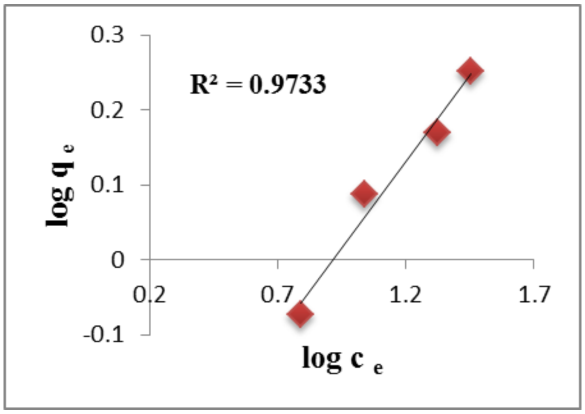

Figure 7 Freundlich adsorption isotherm for Congo red adsorption

Adsorption Kinetics:

In order to investigate the adsorption processes of Congo red onto ash of *Cassia fistula* seeds, the data is subjected to three kinetic models pseudo-first-order, pseudo-second-order and intra-particle diffusion models.

Pseudo-first-order kinetic model:
The pseudo-first-order kinetic model of Lagergren is given by equation:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (5)$$

Where, q_e and q_t are the amount of dye adsorbed at equilibrium and time t (mg/g), K_1 is the pseudo-first order rate constant (min^{-1}). The plot between log (q_e – q_t) verses time t should be a straight line plot if the data follow pseudo-first order kinetic model but the present study do not fit to pseudo-first-order kinetic model.

Pseudo-second-order kinetic model:
The linear equation for pseudo-second-order kinetic model is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (6)$$

Where, K_2 is the pseudo second order rate constant ($g.mg^{-1}.min^{-1}$). The slope and intercept of plot t/q_t verses t has been used to calculate q_e and K_2 and their values are shown in **Table – 3**. The linear plot of t/q_t verses t for pseudo-second-order is shown in **Figure 8**. The value of regression coefficient R^2 is equal to unity which shows that adsorption process of Congo red onto ash of *Cassia fistula* is pseudo-second-order nature.

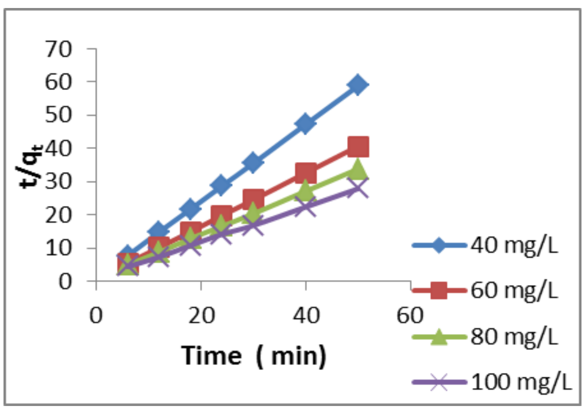

Figure 8 Pseudo-second-order plot for Congo red adsorption

Intra-particle-diffusion model:

The linear equation suggested by Weber and Morris for intra-particle-diffusion model is given by:

$$q_t = K_{ipd}.t^{1/2} + C \quad (7)$$

Where, K_{ipd} is the intra-particle diffusion rate constant (mg g^{-1} min^{-1}) and C is the constant (mg/g). The plot of q_t verses $t_{1/2}$ is shown in **Figure 9**. The intra-particle diffusion rate constant K_{ipd} and C are calculated from the slope and intercept of the plot (**Table - 3**)

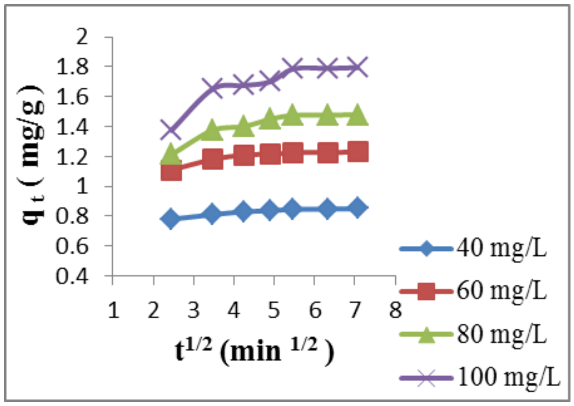

Figure 9 Intra-particle diffusion model for Congo red adsorption

Table 3 Pseudo-second-order and intra-particle-diffusion values

C_0 (mg/L)	Pseudo-second-order calculated			Intra-particle diffusion parameters		
	K_2 (g mg^{-1}min^{-1})	q_e (mg/g)	R^2	K_{ipd} (mg g^{-1}min^{-1})	C (mg/g)	R^2
40	1.7006	0.8618	1.000	0.0146	0.7576	0.860
60	1.2207	1.2478	1.000	0.0231	1.0872	0.754
80	0.4599	1.5283	0.999	0.0531	1.1522	0.788
100	0.2694	1.8733	0.999	0.0811	1.2883	0.781

Thermodynamic parameters:

The thermodynamic parameters, such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) have been evaluated. The free energy change (ΔG) is determined by using the following equation:

$$\Delta G = -RT\ln K_o \quad (8)$$

Where, R is the gas constant and K_o is the equilibrium constant at temperature T. Enthalpy change and entropy change have been evaluated from the Vant't Hofffs equation

$$\ln K_o = \Delta S/R - \Delta H/RT \quad (9)$$

ΔH and ΔS has been calculated from the slope and intercept of the plot between ln K_o verses 1/T. The negative value of ΔG and ΔH shows the feasibility and exothermic nature of adsorption. The negative value of ΔS indicates that entropy decreases at solid-liquid interface. The value of ΔH decreases with increase in initial dye concentration because with increase in concentration there is split in concentration gradient, which leads to desorption of dye particles. At very high concentration the slight increase in enthalpy may be due to the reason that concentration of dye in solution is large, which result in slight decrease in desorption. The low value of enthalpy change indicates the case of physio-sorption.

Table 4 Thermodynamic parameter and equilibrium constant for Congo red adsorption

C_o (mg/L)	K_o			-ΔG (KJ/mol)			-ΔH (KJ/mol)	-ΔS (KJ $mol^{-1}K^{-1}$)
	308 K	313 K	318 K	308 K	313 K	318 K		
40	5.4516	4.7142	3.0000	4.3427	4.0348	2.9045	49.66	0.146
60	4.4545	3.8000	2.7500	3.8254	3.4740	2.6745	40.09	0.117
80	2.8095	2.6363	2.4782	2.6452	2.5223	2.3992	10.43	0.025
100	2.5087	2.1746	2.0303	2.3550	2.0214	1.8721	17.59	0.049

SEM and FT-IR studies:

The adsorption of Congo red on the surface of adsorbent has been confirmed from SEM and FT-IR analysis before and after dye adsorption. The SEM images shown in **Figure 10(a)** and **Figure 10(b)** indicates that before adsorption the surface is rough and porous but after adsorption surfaces of adsorbent has been covered by dye and surface become smooth. The FT-IR spectra (**Figure 11 (a)** and **Figure 11 (b)**) show that there is slight shifting of peaks of adsorbent after adsorption. No new peak has been observed, which indicates that no chemical bond is formed between adsorbate and adsorbent after adsorption, i.e., FT-IR data supports that adsorption of dye on adsorbent is due to physical forces.

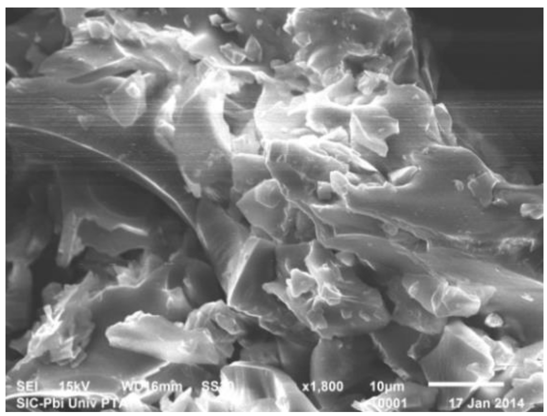

Figure 10 (a) SEM image of ash of *Cassia fistula* before adsorption

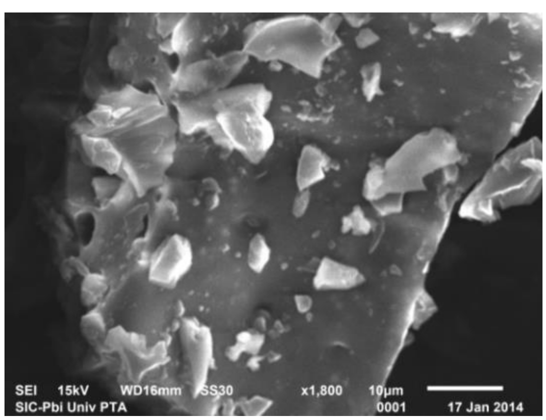

Figure 10 (b): SEM image for ash of *Cassia fistula* after adsorption

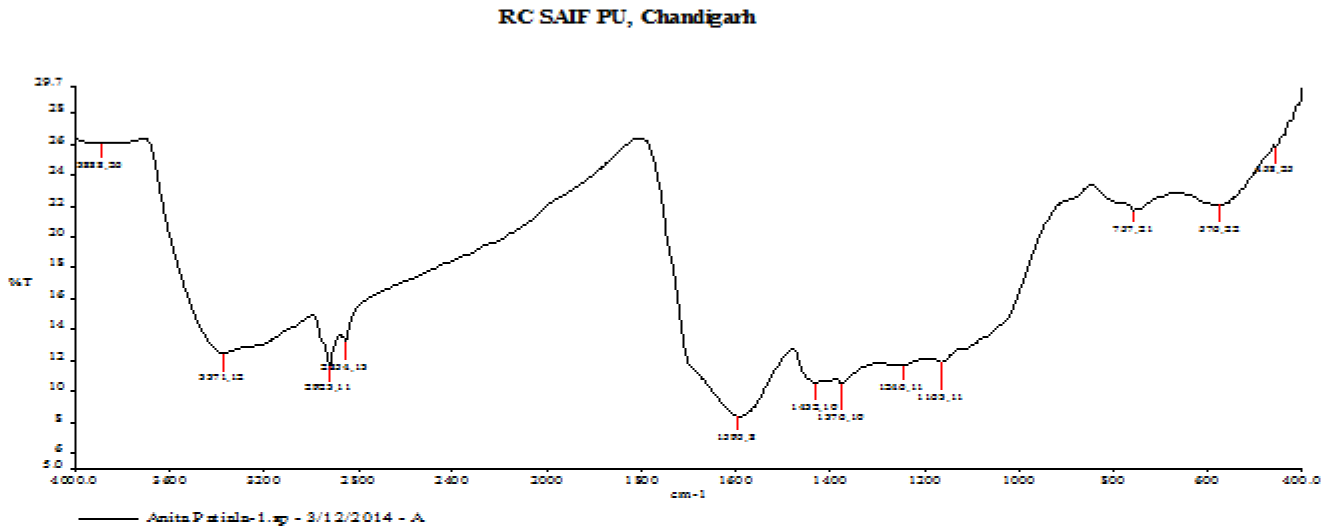

Figure 11 (a) FT-IR spectra of ash of *Cassia fistula* seeds before adsorption

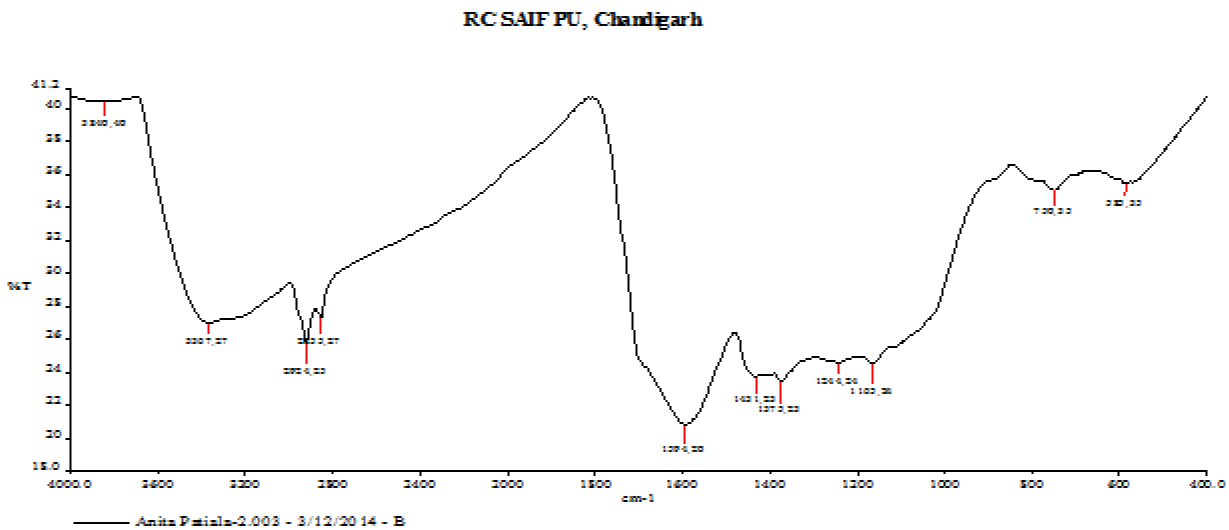

Figure 11 (b) FT-IR spectra of ash of *Cassia fistula* seeds after adsorption.

Conclusion

The present study concluded that (1) Equilibrium has been attained in short time (30 minutes). (2) The adsorption equilibrium correlated reasonably well with the Langmuir and Freundlich isotherm. (3) Data is well fitted to pseudo-second-order and intra-particle-diffusion models. (4) Thermodynamic studies reveals that adsorption of Congo red onto ash of *Cassia fistula* seeds is spontaneous and physical in nature. Thus it is concluded that ash of *Cassia fistula* seeds has considerable potential as an adsorbent for the removal of Congo red dye from aqueous solution.

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