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Sorption Studies of Rhodamine-B by Hibiscus sabdariffa stem Nano Carbon

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Abstract The present research work deals with utilization of Hibiscus sabdariffa stem as an adsorbent for the removal of RhB dyes from the aqueous solutions. The effect of contact time, initial dye concentration, dose of sorbent, chloride ions and pH were considered. Adsorption isotherm data were tested with using Langmuir and Freundlich modes and the adsorption follows both models. The kinetic studies made with pseudo second order, Elovich model and intra- particle diffusion model. Thermodynamic parameters such as ΔH^0, ΔS^0 and ΔG^0 were evaluated which indicated that the adsorption was follows spontaneous and endothermic nature.

Keywords Isotherm, Kinetics, Hibiscus sabdariffa stem Nano Carbon (AHSNC), Rhodamine–B, Thermodynamics.

1. Introduction

A large quantity of highly coloured wastewater effluent is discharged in a large quantity by the textile industries into the nearly assisted lands or river without showing any treatment due to the reason that the conventional treatment was very expensive. At the same time, low cost technologies don't allow a wishful color removal and this lead to certain disadvantages. This is shows that the removal of color from effluents is one of the major environmental problems. The adsorption process has been found to be an effective method for the treatment of dye containing wastewater coagulation, electro coagulation, flotation, chemical oxidation, filtration, ozonation, membrane separation, ion-exchange, aerobic and anaerobic microbial degradation are said to be the possible method of color removal from the textile effluents. All of these methods having any one limitation and none is said to be successful in removing the color from waste water completely [1-2].

2. Material and Methods

2.1 Absorbent

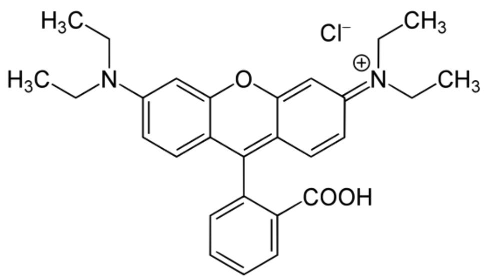
The Hibiscus sabdariffa stem obtained from agricultural area was activated at 110 °C in a muffle furnace for 5 h, then it was taken out ground well to fine powder and stored in a vacuum desiccators.

2.2 Adsorbate

The stock solution of RhB was prepared by dissolving 1 g of dye in 1000 ml of distilled water. The experimental solution say (50 to 250 mg/L) from stock solution by diluting to desired concentrations in accurate proportion. The structural formula of RhB and characteristics are given in Table .1.

Table 1: Characteristics of Rhodamine-B dye

Colour Index No.	45170
Formula	$C_{28} H_{31}N_2O_3Cl$
Formula Weight	479.02
O_{max} (nm)	554
$H(dm^3 \ mol^{-1} \ cm^{-1})$	60000.00



Structure of Rhodamine- B

2.3 Batch adsorption experiments

Batch adsorption experiments were carried out in a mechanical shaker at a constant speed of 150 rpm at 30 °C using with 250 glass- stopper flask contain 25 mg AHSNC with 50 ml of dyes solution at different concentration with various initial pH values the samples were withdrawn from the shaker during agitating flask at present time intervals. The adsorbent were separated from the solution by centrifugation (REMI Make) at 1500 rpm for 50 minutes. The supernatant solution was analyzed to determine the residual dye concentration using UV-Visible spectrophotometer at λ_{max}=553.8.

Dyes amount adsorbed at time t, qt (mg/g) and equilibrium adsorption q_e (mg/g) was calculated from the mass balance principle

$$q_t = (C_i - C_t)V/W \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Where q_t is the amount of dye adsorbed (mg/g) and C_t (mg/L) is the liquid phase concentration of dye at time t, C_0 is the initial concentration of dye solution (mg/L) , V is the volume of the solution (L) , W (g) is the mass of dry adsorbents when t is equal to contact time of equilibrium C_t=C_e q_t=q_e then equation (1) becomes

$$q_e =(C_i - C_e) V/W \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

The amount of dye adsorbed calculated from the equation (2). The dye removal percentage can be determined from the equation (3)

$$R\% = (C_i - C_t) \times 100/ C_i \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

3. Results and Discussion

3.1 Effect of contact time and initial concentrations

The influence of dyes concentration and contact time on the adsorption uptake of RhB with different initial concentration (50 to 250 mg/L), was mixed with 25 mg of AHSNC. The Figure 1 reveals that, the dyes uptake was rapid for first 50 minutes after 50 minutes it was constant with increase in contact time. Based on the results 50 minutes was taken as the contact time to the adsorption process., The equilibrium adsorption capacity (q_e) RhB dyes on to AHSNC increased from 90.856 mg/g to 228.241 mg/g. This result indicates that the initial concentration strongly affects the adsorption capacity.

3.2 Effect of adsorbent dosage

The effect of adsorbent dose was analyzed for the removal of dyes from the aqueous solution. The experiments were investigated by adsorbent dose varied from 10 to 250 mg agitating with 50 ml of different concentration of dye solution. The Figure 2 shows the adsorption of RhB dyes increases rapidly with increase the amount of

Hibiscus sabdariffa stem due to greater availability of the adsorbent surface area at higher concentration of The significant change in RhB dyes was observed when dosage was increased from 10 to 250 mg and the further addition of the sorbent beyond this did not big change in the sorption process. This is due to overlapping of adsorption sites as a result of overcrowding of AHSNC particles [3].

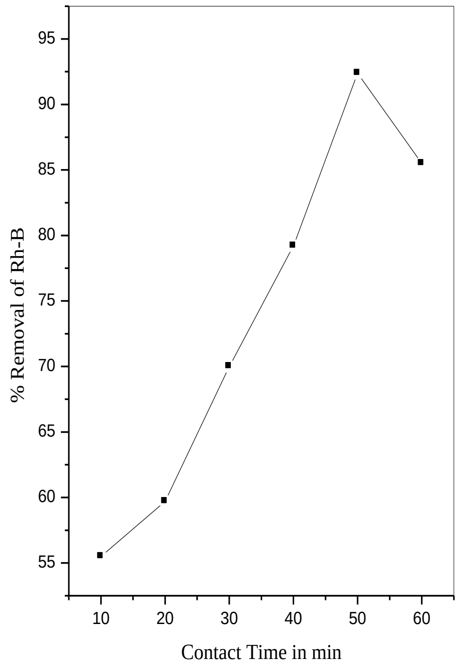
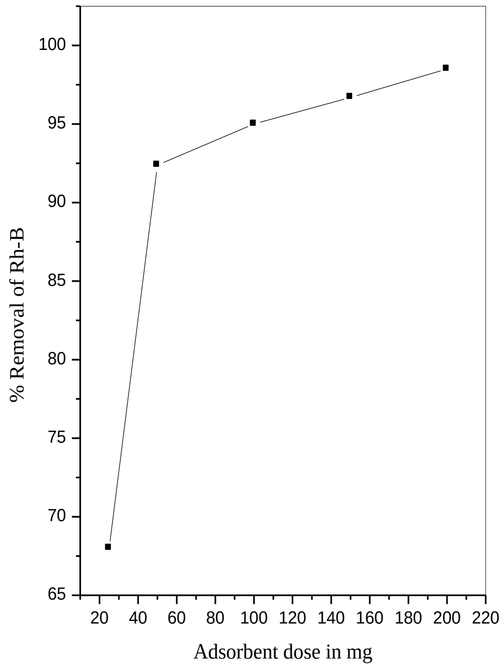
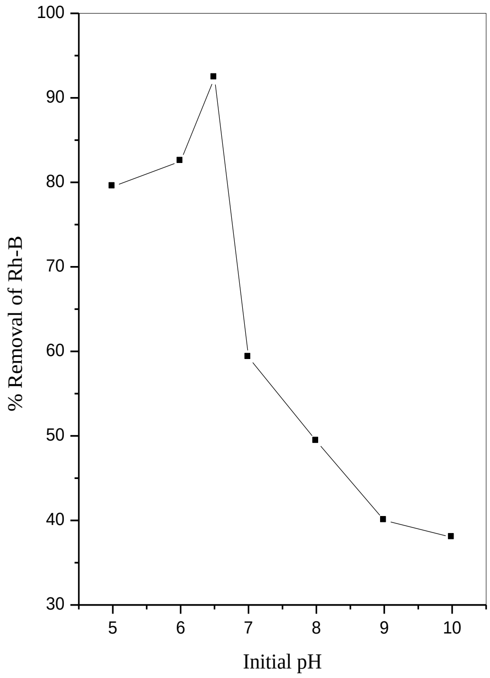


Fig:1- Effect of Contact Time on the Removal of Rh-B
[Rh-B]=50 mg/L;Temprature 30^{o}C;Adsorbent dose=50mg/50ml



Fig;2- Effect of Adsorbent dose on the removal of Rh-B
[RhB]=50mg/L;Contact Time 60min;Temprature 30^{0}C

3.4 Effect of pH



Fig;3- Effect of Initial pH on the removal of Rh-B
[RhB]=50 mg/L;Temprature 30^{o}C;Adsorbent dose=50mg/50ml

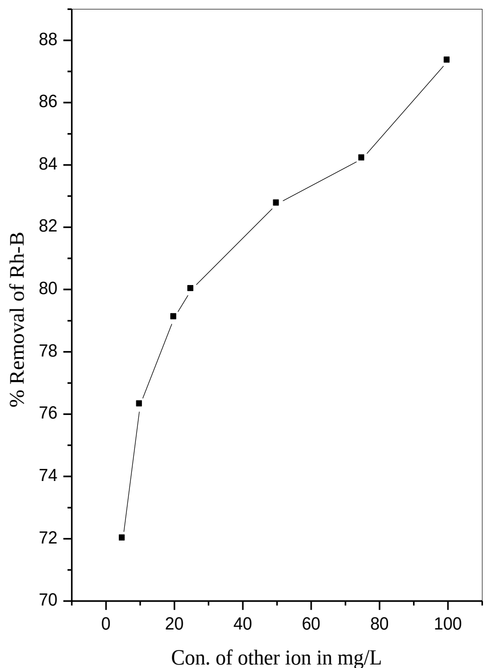


Fig.4-Effect ionic strength on the adsorption of Rh-B
[RhB]=50 mg/L;Contact time=60 min;Dose=50 mg/50 ml

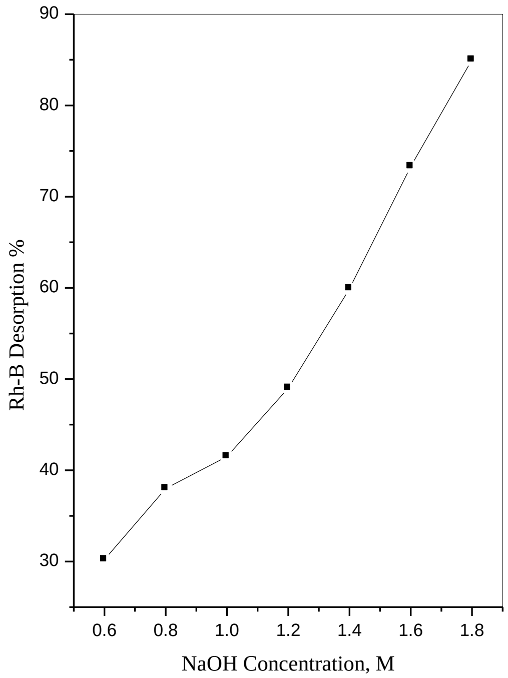


Fig.5- Effect of NaOH Concentration on Rhodamine-B desorption

The pH value of the solution was an important controlling parameter in the adsorption process. The effect of pH on RhB dye adsorption onto Hibiscus sabdariffa stem was analysed over the pH range of 3.0-10.0 and the results are shown in Figure 3. RhB dye adsorption was found to increase with an increase in the initial solution pH. When pH > 6.5 decrease the removal of RhB dye may be due to the occupation sites by anionic species which retards the approach of such ions further towards the adsorbent surface. The experimental results the optimum pH range for the adsorption RhB dye is 2.0 to 6.5.

3.5. Effect of ionic strength

The effect of sodium chloride on the adsorption of Rhodamine-B on AHSNC was studied by the addition of NaCl. The low concentrate NaCl solution had little influence on the adsorption capacity. When the concentration of NaCl increases, the ionic strength is raised. At higher ionic strength, the adsorption of Rhodamine-B will be high owing to the partial neutralization of the positive charge on the AHSNC surface and a consequent compression of the electrical double layer by the Cl^- anion. The chloride ion also enhances adsorption of Rhodamine -B ion by pairing their charges, and hence reducing the repulsion between the RhB molecules adsorbed on the surface. This initiates AHSNC to adsorb more positive Rhodamine-B ions [4-7].

Table 2: Equilibrium parameters for adsorption of RhB dye onto AHSNC

C_0	Ce (Mg / L)				Qe (Mg / g)				R (%)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
50	4.2260	3.6720	3.1988	2.905	91.5480	92.656	93.602	94.189	91.548	92.656	93.602	94.189
100	20.006	17.660	14.500	12.23	159.99	164.68	171.00	175.53	79.994	82.340	85.500	87.765
150	44.761	39.534	34.514	30.08	210.48	220.93	230.97	239.84	70.159	73.644	76.991	79.946
200	87.074	80.448	34.514	66.57	225.85	239.10	330.97	266.85	56.463	59.776	82.743	66.713
250	135.87	127.49	73.484	111.4	228.25	245.03	353.03	277.19	45.650	49.005	70.606	55.438

3.5. Adsorption isotherms

The distribution of dyes between the liquid phase and solid phase can be described by several isotherm such as Langmuir, Freundlich isotherm equation have been used in this study.

Table 3: Langmuir and Freundlich isotherm parameter for adsorption of RhB on to AHSNC

Temperature °C	Langumuir parameter		Fruendlich parameter	
	Q_0	b	K_f	n
30	243.03	0.1259	66.218	3.6498
40	260.99	0.1255	68.834	3.5223
50	423.20	0.0584	55.815	2.2775
60	294.89	0.1407	75.603	3.3256

3.5.1. Langmuir isotherm

The Langmuir model assumes that the uptake of dye occurs on the homogeneous surface by monolayer adsorption without any interaction between adsorbed dyes. The Langmuir isotherm [8] has been represented as

$$C_e/ q_e =(1/ Q_0 b) +(C_e/ Q_0) \text{-------------------------- (4)}$$

Where q_e (mg/g) is the amount of dye adsorbed onto per unit mass Langmuir isotherm model confirm the homogeneous nature of Hibiscus sabdariffa stem. The results also enhance the formation monolayer coverage of RhB dye molecule at surface of AHSNC, similar results reported by adsorption of cango red dye on activated carbon from coir pith [9-10] by the adsorption direct dyes of adsorbent to form complete monolayer on the sorbent surface, Ce (mg/L) is the equilibrium concentration of the dye ions, Q_0 (mg/g) and b (mg/L) are Langmuir constants related to the adsorption and energy of adsorption respectively. The plot of Ce/qe against Ce gives straight line. The constant Q_0 and b can be calculated from the slope and intercept and their values are given in Table 3. This indicates that the adsorption of RhB on to Hibiscus sabdariffa stem follows the Langmuir isotherm. The essential feature of the Langmuir isotherm can be explained in terms of a dimensionless equilibrium parameter which is defined by following equation [11-12].

$$R_L = 1/1+bC_0 \text{ -------------------- (5)}$$

where b (L/mg) is the Langmuir constants related to the energy of adsorption and C_0 is the initial dye concentration (mg/L).The values of R_L indicate the types of isotherm process and given as below

R_L values	Adsorption
$R_L > 1$	Unfavourable
$R_L =1$	Linear
$0 < R_L <1$	Favourable
$R_L =0$	Irreversible

3.5.2. Freundlich isotherm model

The Freundlich isotherm is an empirical equation. It is based on multilayer adsorption on heterogeneous surface [13] the linear form of Freundlich equation is given as

$$\log q_e = \log k_f +1/n \log C_e \text{ ---------------------(6)}$$

where q_e is the amount of dye adsorbed at per unit gram of adsorbent (mg/L), Ce is the equilibrium concentration in solution after adsorption(mg/L), K_f (mg/g(L/mg) is the Freundlich constant related to binding energy and n (g/L) is the heterogeneity factor. The values of K_f and n were obtained from the intercepts (log k_f) and slope (1/n) of the plot of log q_e vs log C_e values of K_f and n are given the Table 3. The values of 1/n is less than unity, it is indicate favorable adsorption [14]. The plot of log q_e versus log C_e gives a straight line with slope 1/n which indicates that the adsorption of RhB on to AHSNC follows the Freundlich isotherm mode.

3.6. Thermodynamics Parameters

Thermodynamic parameters like ΔH^0, ΔS^0 and ΔG^0 can be determined at different temperature namely 303, 313, 323 and 333 K by using the following relations

$$K0= Cad / Ce \text{ ------------------------ (7)}$$

$$\Delta G0 = -RT\ln K_0 \text{ ------------------------ (8)}$$

$$\log K_o = \Delta S^0 /2.303R - \Delta H^0/2.303RT \text{ ---------- (9)}$$

Where K_0 is the equilibrium constant, Cad is the solid phase concentration at equilibrium (mg/L), Ce is the equilibrium concentration of the dye solution (mg/L), and R is the gas constant T is the absolute solution temperature in Kelvin. The ΔH^0 and ΔS^0 values for dye sorption can be determined from the slope and intercept of the linear plot of $\log K_0$ Vs 1/T. The values are presented in Table 4. The positive values of ΔH^0 confirm the endothermic adsorption of RhB on to AHSNC. The more negative values of ΔG^0 indicate the feasibility of dye process is spontaneous nature. The positive values of ΔS^0 shows the increased randomness at the solid – solution interface. In desorption of dye the adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than it is lost by the adsorbate molecules, thus allowing prevalence of randomness in the system [15-16].

Table 4: Dimensionless seperation factor (RL) for adsorption of RhB on to AHSNC

Initial Concentration (C_0)	Temperature °C			
	30°C	40°C	50°C	60°C
50	0.1371	0.1375	0.2551	0.1244
100	0.0736	0.0738	0.1462	0.0663
150	0.0503	0.0504	0.1024	0.0452
200	0.0382	0.0383	0.0788	0.0343
250	0.0308	0.0309	0.0641	0.0276

Table 5: Thermodynamic parameter for the adsorption of RhB on to AHSNC

C_0	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
50	-6001.8	-6596.8	-7205.4	-7712.2	11.408	57.507
100	-3491.3	-4006.3	-4764.9	-5455.0	16.644	66.269
150	-2153.6	-2673.9	-3243.4	-3828.7	14.790	55.865
200	-654.9	-1030.9	-4209.4	-1924.8	21.285	73.084
250	439.4	103.6	-2353.3	-604.6	17.967	58.399

3.7. Pseudo- second – order kinetic model

The linear form of the pseudo second order kinetic rate equation [17] is expressed as

$$t/q_t = 1/K_{2ad}\, qe^2 + 1/q_e\,(t) \quad \text{………………}(10)$$

Where k_2 (g/mg min) is the second order rate constant, q_e is the amount of dye adsorbed on the per unit mass of adsorbent (mg/g) at equilibrium, q_t is the amount of dye adsorbed at time t, per unit mass of adsorbent(mg/g). The values of k_2 and equilibrium capacity (q_e) can be calculated from the slope and intercepts of the curve plot of t/qt versus 1/qe. The second – order rate constant k_2, calculated h values and (γ) values are given in table 6. A plot of t/qt versus $1/q_e$ gives a straight line. It reveals that the adsorption process follows pseudo- second- order kinetics model.

3.8. The Elovich equation

The Elovich model is a rate equation, for the absorbing surface is heterogeneous [18-19]. It is generally represented as

$$dq_t / d_t = \alpha \exp(-\beta q_t) \quad \text{……………} \quad (11)$$

where, α is the initial adsorption ($mg.g^{-1}min^{-1}$),β is the adsorption constant(g/mg) during any one experiment. To simply the Elovich equation, assumed α βt >> T and by applying the boundary conditions q_t= 0 at t=0 and q_t=q_t at t=t equation (11) becomes

$$q_t = 1/\beta \ \ln(\alpha\beta) + 1/\beta \ln(t) \text{ ……………………}(12)$$

A plot of ln q_t vs ln t should yield a linear trace with a slope of (1/ β) and an intercept of (1/β) ln (αβ). The plots are linear with good correlation coefficient and the results are tabulated in Table.6.

3.9. The intra- particle diffusion model

The intra- particle diffusion model from Weber and Morris [20] following equation

$$q_t = k_{ipd}\,.t^{1/2} + Ci \text{ ----------------------- } (12)$$

Where K_{ipd} is the intra–particle diffusion rate constant (mg/g min), q_t is the amount of dye adsorbed on to adsorbent at time t (mg/g), C_i is the intercept given an idea about the thickness of the boundary layer. The plot of qtagainst $t^{1/2}$ gives a multi-linearity,. it is shows two linear portion the first part curve attributed to boundary layer diffusion while the final liner part shows intra- particle diffusion. Where the line does not pass through the origin indicating that intra-particle involved in the adsorption process but it is not involved in the rate limiting steps the diffusion parameters present in Table 6.

Table 6: The kinetic parameter for adsorption of RhB dye on to AHSNC

C_0	Temp	Pseudo second order				Elovich model			Intraparticle diffusion		
	°C	q_e	k_{2ad}	γ	h	α	β	γ	K_{IPD}	γ	Ci
50	30	108.87	0.0007	0.9858	8.403	26.60	0.0487	0.9899	0.2726	0.9910	1.4690
	40	108.60	0.0008	0.9878	9.017	32.51	0.0509	0.9920	0.2546	0.9931	1.5046
	50	108.28	0.0008	0.9850	9.749	40.41	0.0533	0.9891	0.2383	0.9902	1.5377
	60	109.19	0.0008	0.9860	9.754	39.31	0.0524	0.9902	0.2411	0.9913	1.5361
100	30	194.12	0.0003	0.9852	13.143	36.03	0.0259	0.9893	0.3000	0.9904	1.3603
	40	197.85	0.0004	0.9862	14.041	41.66	0.0262	0.9904	0.2853	0.9915	1.3975
	50	201.83	0.0004	0.9854	16.065	53.50	0.0267	0.9895	0.2652	0.9906	1.4514
	60	207.13	0.0004	0.9874	16.831	56.07	0.0260	0.9916	0.2643	0.9927	1.4663
150	30	268.92	0.0002	0.9856	14.229	33.02	0.0174	0.9897	0.3509	0.9908	1.2115
	40	274.15	0.0002	0.9849	16.588	41.53	0.0176	0.9890	0.3234	0.9901	1.2824
	50	282.43	0.0002	0.9849	19.015	51.30	0.0177	0.9890	0.3028	0.9901	1.3418
	60	288.81	0.0002	0.9867	16.376	55.56	0.0189	0.9909	0.2756	0.9920	1.3725
200	30	330.68	0.0001	0.9851	10.752	21.73	0.0131	0.9892	0.4695	0.9903	0.9057
	40	334.02	0.0001	0.9861	12.540	25.84	0.0131	0.9903	0.4325	0.9914	0.9956
	50	340.09	0.0001	0.9872	14.648	31.13	0.0131	0.9914	0.3996	0.9925	1.0793
	60	343.90	0.0002	0.9863	17.922	40.31	0.0134	0.9905	0.3607	0.9916	1.1758
250	30	442.79	0.0000	0.9887	7.378	15.76	0.0106	0.9929	0.6354	0.9940	0.5203
	40	429.29	0.0000	0.9888	8.786	18.18	0.0104	0.9930	0.5853	0.9941	0.6380
	50	444.24	0.0000	0.9874	9.717	19.99	0.0100	0.9916	0.5650	0.9927	0.7007
	60	420.91	0.0001	0.9881	12.281	24.62	0.0102	0.9923	0.5010	0.9934	0.8422

Conclusion

The experimental results show that the Hibiscus sabdariffa stem for the adsorption of RhB dye was effective. The maximum adsorption of RhB dye adsorption was increased with increase in the dosage of sorbent and decreasing increasing with initial concentration. The adsorption data's were well fit in both Freundlich and Langmuir model and was well described by pseudo- second–order kinetics model. A series of experiments were conducted by batch system and it was observed that more than 90% of dye removal was archived by using 25 mg of Hibiscus sabdariffa stem .

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