



EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDY ON RHODAMINE-B REMOVAL FROM AQUEOUS SOLUTION USING ACTIVATED CORCHORUS OLITORIUS-L LEAVES

S Subasri^{1*}, S Arivoli^{2*}, V Marimuthu² and N Mani¹

^{1*}Department of Chemistry A.V.V.M Sri Pushpam College, Poondi, Thanjavur, Tamil Nadu, India.

^{2*}Department of Chemistry, Thiru. Vi.Ka. Government Arts College Thiruvavur, Tamil Nadu, India.

*Authors for Correspondence:arivu3636@yahoo.com, srisuba123@gmail.com.

ABSTRACT: The research of the present work was to investigate the removal of Rhodamine-B dye from aqueous solution by using *Corchorus Olitorius-L* Leaves Nano Carbon (ACONC). Generally, dyes are used in chemical, textile, paper, printing, leather, plastics and various food industries. The need for the treatment of dye contaminated waste water passed out from the industry. In this study, *Corchorus Olitorius L* Nano Carbon was studied for its potential use as an adsorbent for removal of Rhodamine-B dye. The various factors affecting adsorption, such as initial dye concentration, contact time, adsorbent dose, effect of temperature and pH were evaluated. The experimental data were fitted into the pseudo-second order kinetic model. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherm models. The objective of the present work suggests the ACONC may be utilized as a low cost adsorbent for Rhodamine-B dyeremoval from aqueous solution.

Key words: Activated *Corchorus Olitorius L* Nano Carbon (ACONC); Rh-B dye; Adsorption isotherm; Kinetics; Equilibrium models.

INTRODUCTION

With the revolution in textile industries discharge colored effluents such as organic dyes like Methylene Blue and Rhodamine-B to water bodies. These colored effluents have large amounts of suspended organic solids which are harmful to human beings and toxic for organisms. The removal of these dyes from wastewater has a considerable attention over the past decades to decrease their impact on the environment, as discussed elsewhere [1]. Several physical and chemical methods have been developed for the removal of organic dyes from industrial effluents. Physical methods, mainly adsorption on various supports were recognized to be a promising and effective process to remove dyes from industrial waste waters completely, as discussed elsewhere [2, 3]. The main advantages of adsorption are the reusability of material, low-cost, ease of operation and short time of operation so it is necessary to develop effective adsorbents for the removal of dyes from textile effluents. Activated carbon is the most widely used adsorbent and can be prepared by physical activation in which carbonation or pyrolysis of the carbonaceous material at higher temperature (500-900°C) in an inert atmosphere followed by thermal activation at the same temperature in the presence of oxidizing agent such as air, steam and carbon dioxide or chemical activation in which pyrolysis and activation carried out only in one step simultaneously in presence of dehydrating agent such as H₃PO₄, HNO₃, KOH, NaOH, H₂O₂, H₂SO₄. Chemically activated carbon has higher yield, more surface area and better development of porous structure than that obtained by physical activation, as discussed elsewhere [4, 5]. Several attempts have been studied for the preparation of activated carbon from agriculture wastes.

In this article, we have reported the use of natural bio materials is an alternative due to their relative abundance and their low commercial values. *Corchorus Olitorius L* is the most ancient plant of India. It is found through out India, especially in Tamil Nadu, Kerala, Bengal and solve south region, the aerial parts of the tree have medicinal values and this work studied the possibility of using fallen leaves of a *Corchorus Olitorius L* plant as an adsorbent for the adsorption of cationic dye Rhodamine-B from aqueous solution. A survey of literature shows that no work has been done so far for a vitalization of fallen *Corchorus Olitorius L* plant leaves as an adsorbent.

MATERIALS AND METHODS

All reagents used in the experiments were of analytical (AR) grade and were obtained from scientific equipment Company Trichy. Stock solutions of the test reagents were prepared by dissolving the dye in distilled water.

Preparation of adsorbent

The natural plant material for *Corchorus Olitorius L* Leaves used in the present investigations was collected from a nearby Thiruvarur. The leaf was washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110°C. Afterward, carbonization of the leaves was carried out by adding w/v ratio $\text{Con.H}_2\text{SO}_4$ to get the primary carbon. The primary carbon was activated at 1200 °C for 6 hrs under optimized conditions to obtain the activated nano carbon.



Corchorusolitorius - L. (Jew's Mallow)

Experimental Procedure

Batch experiments were conducted to study the influence of important parameters like the pH, contact time, initial dye concentration and temperature on the removal of Rh-B onto activated *Corchorus Olitorius L* Nano Carbon. For Adsorption Isotherms, dye solution of different concentrations (50-250 mg/L) and at different temperatures (30-60 °C) with known pH and known amount of adsorbent (0.5 g/L) were agitated at 120rpm until the equilibrium was reached then the solution was kept to settle down and the residual concentration of Rh-B were analyzed by UV-Visible spectrophotometer at 662 nm and 554 nm, respectively. All experiments were carried out at normal pH for Rh-B. Effect of pH on dye removal was studied over a pH range of 2.0-10.0 the initial pH of the solution was adjusted by addition of acetate or phosphate buffers. The effect of sorbent dosage on adsorption rate was investigated using the procedures described above except that different dosages (50–250 mg/50ml) were used. The percentage of dye removal was calculated using the following equation.

$$q_{(t)} = \frac{((C_{(i)} - C_{(t)}) \times V)}{m} \quad (1)$$

Where, $q_{(t)}$ is the mass of adsorbed dye per unit mass of adsorbent (mg g^{-1}) (i) and (t) are the initial and actual concentration (g dm^{-3}) of dye at time, respectively V is the volume of the treated solution (ml) m is the mass of adsorbent (g) The adsorption degree, AD as a function of time was also determined from the experimental data using the following relationship

$$\text{AD \%} = \frac{(1 - C_{(t)}) \times 100}{C_i} \quad (2)$$

Based on the adsorption kinetics experiments, the process time for the equilibrium adsorption experiments was chosen, long enough assuming that the considered sorbent / sorbate system is equilibrated. The following parameters of the process were changed during these experiments kind and amount of adsorbent (Activated *Corchorus Olitorius L*) the particle size: The initial pH of the solutions and the initial concentration of the considered ions, all experiments were performed at ambient temperature.

RESULT AND DISCUSSION

Characterization.

The different chemical constituents of activated *Corchorus Olitorius L* Nano Carbon are given in Table 1 along with some other characteristics. Surface area of the samples activated in air is 527 and 96 $\text{m}^2 \text{g}^{-1}$ for Activated *Corchorus Olitorius L*, respectively. X-ray spectra of both adsorbents do not show any peak indicating the amorphous nature of activated *Corchorus Olitorius L* nano carbon.

Table 1-Characteristics of the Adsorbent

Properties	ACONC
Particle size(mm)	0.010
Density (g/cc)	0.2125
Moisture content (%)	0.1827
Loss in ignition (%)	0.019
pH of aqueous solution	5.0

Contact time

In order to establish the equilibration time for maximum uptake and to know the kinetics of the adsorption process, Rh-B adsorption on ACONC adsorbent was investigated as a function of contact time and the results shown in fig 1. The figure shows that the uptake rate was initially rapid with 50% of the adsorption was complete with in 30min, Equilibrium was achieved within 50min therefore, an equilibration period of 1 h was selected for all further experiments. The time profile of RhB uptake is a single Smooth and continuous curve leading to saturation suggesting the possible monolayer coverage of Rh-B on the surface of the adsorbent, as discussed elsewhere [6, 7].

Effect of adsorbent dosage

The adsorption of the Rh-B dye on ACONC was studied by varying the adsorbent dose (25–250 mg/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased with increases in the ACONC dose, which is attributed to increased carbon surface area and the availability of more adsorption sites, as discussed elsewhere [8, 9]. Hence, all studies were carried out with 0.025g of adsorbent/50 ml of the varying adsorbate solutions. 50, 100, 150, 200 and 250. The Results obtained from this study are shown in figure 2. The amount of Rh-B adsorbed per gram reduced with increase in the dosage of ACONC. This reveals that the direct and equilibrium capacities of Rh-B are functions of the activated ACONC dosage.

Effect of Initial pH.

Previous research has shown that the adsorption of dye molecules onto an adsorbent is highly pH dependent since, the functional groups, which are responsible for interaction between dye molecules and adsorbent, can be protonated or deprotonated to produce different surface charges in solution at different pH values. Therefore the effects of initial solution pH were studied in the pH range of 2-10 for Rh-B. The percentage removal increased from 63 % to 92 % for Rh-B whereas it decreased slowly after pH 8 for Rh-B Fig 3. The pH_{zpc} of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. It is well-known that for basic dye adsorption, negatively charged groups on the adsorbent are necessary, as discussed elsewhere [10]. At lower pH values ($pH < pH_{zpc}$) the surface charge of the surface of ACONC may get positively charged as a result of being surrounded by H_3O^+ ions and thus the competitive effects of H_3O^+ ions as well as the electrostatic repulsion between the dye molecules and the positively charged active adsorption sites on the surface of the ACONC lead to a decrease in the uptake of dye molecules. In contrast at higher pH values ($pH > pH_{zpc}$) the surface of ACONC may acquire a negative charge leading to an increase in dye uptake due to the electrostatic force of attraction. On the other hand no valid reason can be given for the decrease in the adsorption amount of RhB after pH 8. Similar results were obtained for the adsorption of Rhodamine-B onto Activated Corchorus Olitorius L. As a result, the initial pH value was optimized as 7.0 for dye.

Effect of other ions

The effect of other ions like Ca^{2+} and Cl^- on the adsorption process studied at different concentrations. The ions added to 50mg/L of Rh-B solutions and the contents were agitated for 60 min at 30°C. The results had shown in the Fig. 4 reveals that low concentration of Cl^- does not affect the percentage of adsorption of Rh-B on ACONC, because the interaction of Cl^- at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion Ca^{2+} increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases that, decreases the percentage adsorption. The interference was more in the presence of Ca^{2+} compared with Cl^- ion. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions, as discussed elsewhere [11].

Adsorption Models

The adsorption equilibrium data were further analyzed into two well known isotherm models via Freundlich and Langmuir models.

Freundlich model

The Freundlich model which is an indicative of surface heterogeneity of the adsorbent is described by the following equation, as discussed elsewhere [12].

$$\text{Log } q_e = \log k_f + (1/n) \log C_e \quad (3)$$

Where K_f and $1/n$ are Freundlich constants associated with adsorption capacity and adsorption intensity respectively, The Freundlich plots between $\log q_e$ and $\log C_e$ for the adsorption of Rh-B were drawn. It was found that correlation coefficient values were less than 0.99 at both the temperature studied indicating that Freundlich model was not applicable to the present study.

Langmuir model

The adsorption isotherm was also fitted to Langmuir model, as discussed elsewhere [13]. The Langmuir equation which is valid for monolayer adsorption on to a surface is given below.

$$1/q_e = 1/q_m + 1/q_m b C_e \quad (4)$$

Where, q_e (mgg^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mol L^{-1}), q_m (mgg^{-1}) is the Langmuir constant representing the maximum monolayer adsorption capacity and b (Lmol^{-1}) is the Langmuir constant related to energy of adsorption. The plots $1/q_e$ as a function of $1/C_e$ for the adsorption of Rh-B was found linear. Suggesting the (table 3) applicability if Langmuir model in the present adsorption system. The correlation coefficient ($R^2 = 0.9926$ to 0.9932 at 30 to 60°C respectively for Langmuir model) confirm good agreement between both theoretical models and our experimental results the values of the monolayer capacity (q_m) and equilibrium constant (b) have been evaluated from the intercept and slope of these plots and given in Table 3. It is adsorbent for the Rh-B is comparable to the maximum adsorption obtained from the adsorption isotherms. These facts suggest that Rh-B is adsorbed in the form of monolayer coverage on the surface of the prepared adsorbent. Satisfactory fitting of the Langmuir model to the adsorption of Rh-B on Activated *Corchorus Olitorius L* nano carbon adsorbent. The Langmuir constant Q_m and b were determined from the slope and intercept of the plot and are presented in table 3. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L , as discussed elsewhere [14] by the equation

$$R_L = (1/(1+bC_0)) \quad (5)$$

Where C_0 (mg/L) is the highest initial concentration of adsorbent and b (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

$R_L > 1$ Unfavorable adsorption

$0 < R_L < 1$ Favorable adsorption

$R_L = 0$ Irreversible adsorption

$R_L = 1$ Linear adsorption

The R_L values between 0 to 1 indicate favorable adsorption for all initial concentration (C_0) and temperatures studied. The calculated R_L values are given in table 4. The values of b were increased with increasing the dose of adsorbent for ACONC. High b values indicate high adsorption affinity the monolayer saturation capacity Q_m were around 361 mg/L for ACONC.

Table: 2. Equilibrium Parameters for the Adsorption of Rh-B on to Corchorus Olitorius L

M_0	C_e (Mg / L)				Q_e (Mg / L)				Removal %			
	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	3.44	3.23	3.20	3.10	91.39	92.72	92.53	93.98	92.12	92.30	93.53	93.28
100	12.26	12.36	10.73	9.08	171.47	173.27	178.53	181.83	86.73	87.63	91.26	90.51
150	31.36	25.64	23.59	21.68	239.26	245.70	253.80	258.62	80.75	83.50	84.60	86.55
200	56.62	54.09	23.09	44.70	282.74	281.81	343.20	310.58	71.68	72.95	88.25	78.64
250	91.67	88.58	49.06	74.68	318.65	328.02	421.87	350.63	63.73	65.72	80.37	73.12

Table: 3. Langmuir and Freundlich Isotherm Parameter for the adsorption OF Rh-B onto Corchorus Olitorius L

Temp. (°C)	Langmuir Parameters		Freundlich Parameters	
	Q_m	b	K_f	n
30°C	350.73	0.0713	1.7203	2.5411
40°C	378.39	0.0743	1.7333	2.4949
50°C	572.69	0.0454	1.6200	1.8632
60°C	385.60	0.0920	1.8168	2.3673

Table: 4. Dimensionless Separation Factor (R_L) for the Adsorption OF Rh-B onto Corchorus Olitorius L

(C_i)	Temperature °C			
	30°C	40°C	50°C	60°C
50	0.2114	0.2106	0.3211	0.1723
100	0.1344	0.1271	0.1812	0.0940
150	0.0965	0.0832	0.1356	0.0621
200	0.0563	0.0601	0.0962	0.0514
250	0.0568	0.0533	0.0723	0.0507

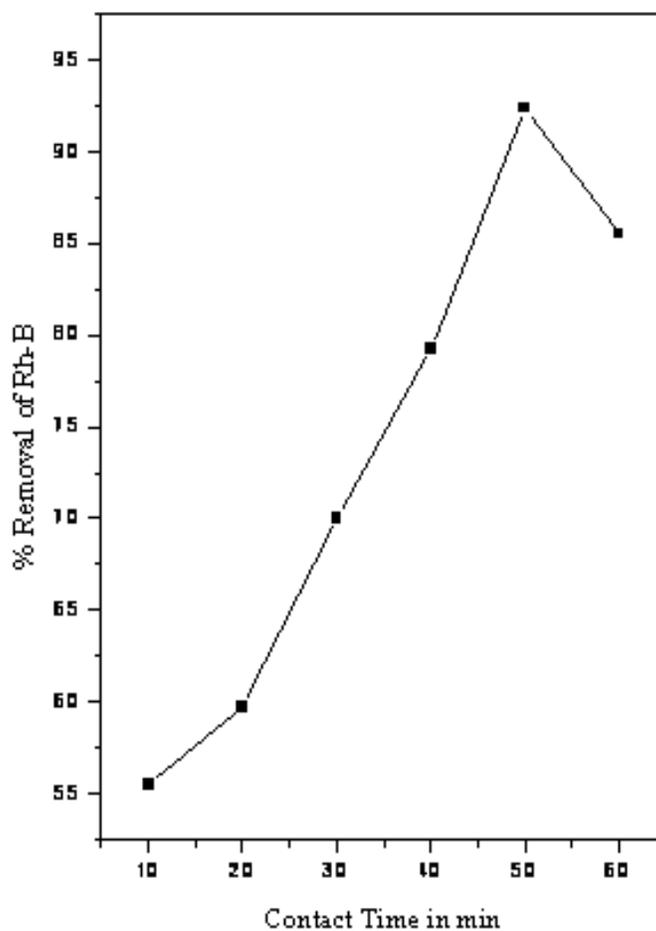


Figure-1: Effect of Contact time on the removal of Rh-B [RhB]=50 mg/L, Temperature 30°C, Adsorbent dose = 50 mg/50 ml

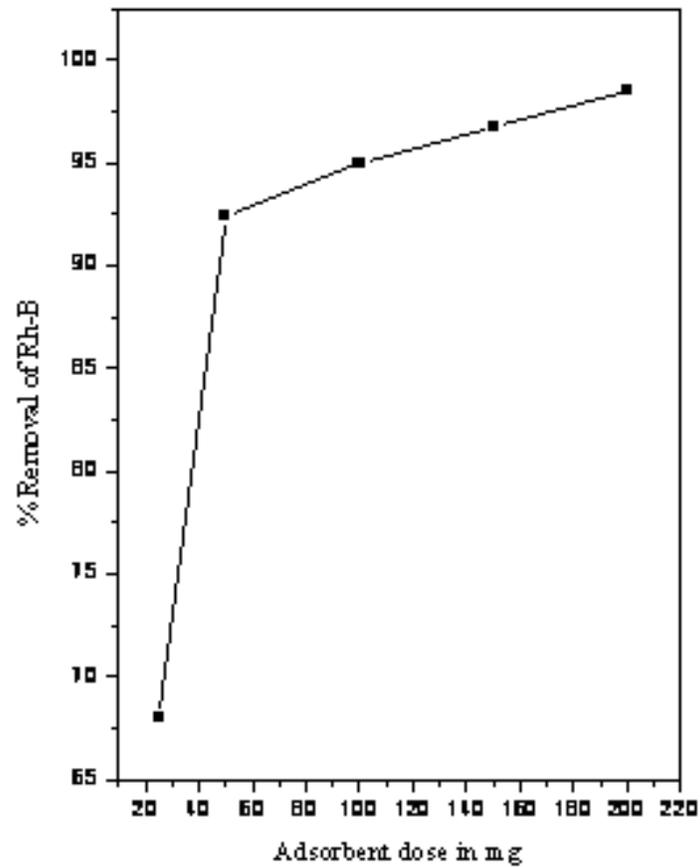


Figure-2: Effect of Adsorbent dose on the removal of Rh-B [RhB]=50 mg/L, Contact time=60 min, Temperature 30°C

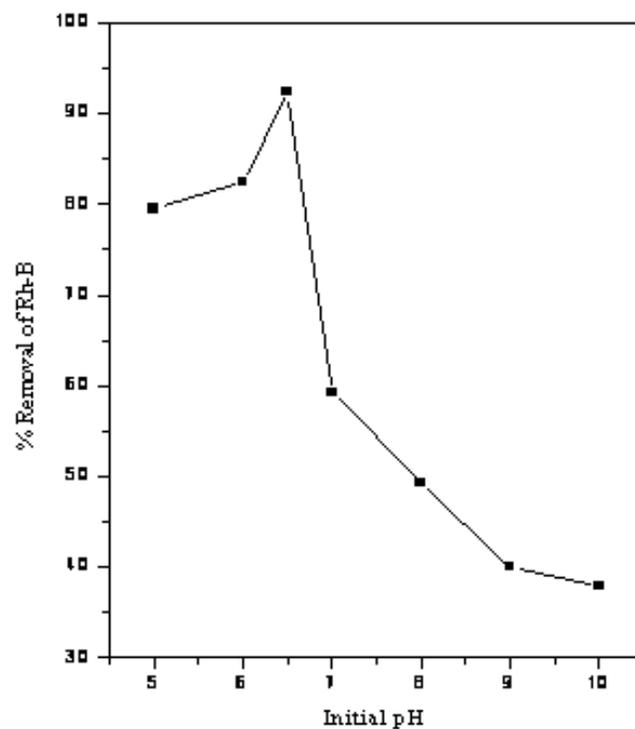


Figure-3: Effect of Initial pH on the removal of Rh-B [RhB]=50 mg/L, Temperature 30°C, Adsorbent dose = 50 mg/50 ml

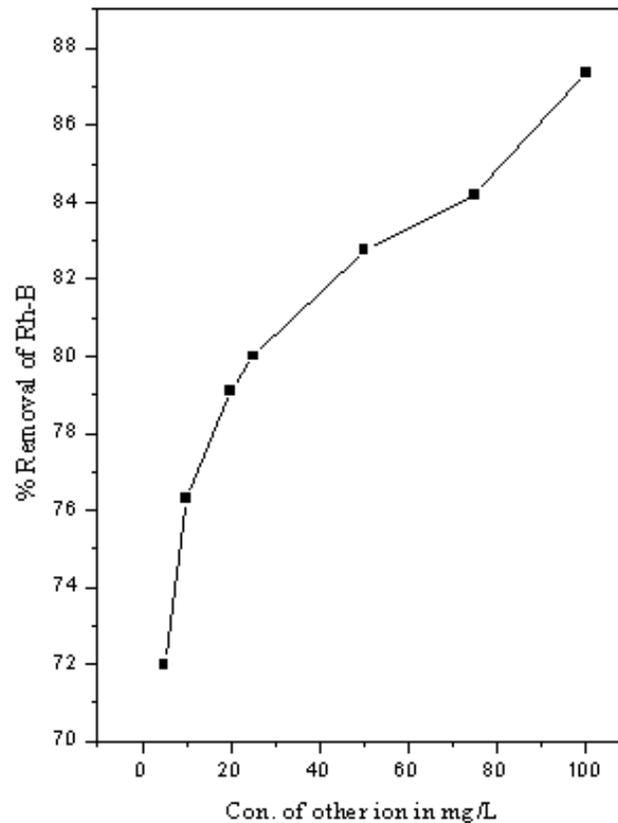


Figure-4: Effect of ionic strength on the adsorption of Rh-B [RhB] = 50 mg/L, Contact time=60 min, Dose=50 mg/50 ml

Thermodynamic treatment of the adsorption process

Thermodynamic parameters associated with the adsorption, via standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant K_0 is given by the equation:

$$\Delta G^0 = -RT \ln K_0 \quad (6)$$

Where ΔG^0 is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 J mol/K). The adsorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot of $\ln(q_e/C_e)$ against C_e at different temperature and extrapolating to zero C_e according to the method as discussed by Khan and Singh [15]. The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH^0) and entropy change (ΔS^0) as a function of temperature,

$$\ln K_0 = (\Delta H^0/RT) + (\Delta S^0/R) \quad (7)$$

Where ΔH^0 is the standard heat change of sorption (kJ/mol) and ΔS^0 is standard entropy change (kJ/mol). The value of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of plot of $\ln K_0$ against $1/T$. The value of thermodynamic parameter calculated from equation 6 and 7 are shown in table 5. The thermodynamic treatment of the sorption data indicates that ΔG^0 values were negative at all temperature. The results point out that physisorption is much more favorable for the adsorption of Rh-B dye. The positive values of ΔH^0 show the endothermic nature of adsorption and it governs the possibility of physical adsorption [16]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of Rh-B adsorption increases, this rules out the possibility of chemisorptions [17]. The low ΔH^0 value depicts Rh-B dye is physisorbed onto adsorbent ACONC.

The negative ΔG^0 values (table 5) was confirm the spontaneous nature of adsorption Rh-B dye onto ACONC. The lesser values of ΔG^0 suggest that adsorption is physical adsorption process. The positive value of ΔH^0 further confirms the endothermic nature of adsorption process. The positive values of ΔS^0 in table 5, showed increased randomness of the solid solution interface during the adsorption of copper ion onto Activated Corchorus Olitorius Nano Carbon.

Table: 5. Thermodynamic Parameter for the Adsorption of Rh-B onto Corchorus Olitorius L

(C ₀)	ΔG°				ΔH°	ΔS°
	30°C	40°C	50°C	60°C		
50	-6359.62	-6523.7	-6749.89	-7312.5	6.019	39.41
100	-4228.22	-5086.11	-5289.3	-6347.31	14.19	60.56
150	-3553.76	-3860.54	-4525.28	-5054.15	13.99	54.54
200	-2214.31	-2522.12	-5467.31	-3447.26	17.39	63.61
250	-1350.07	-1294.32	-3726.12	-2332.47	15.97	54.23

Table: 5. The Kinetic Parameters for Adsorption for the adsorption of Rh-B onto Corchorus Olitorius L

C ₀	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q _e	K ₂	γ	h	α	β	γ	K _{id}	γ	C
50	30	102.15	21×10 ⁻³	0.9952	14.01	134.90	0.0694	0.9959	1.6461	0.994	0.1771
	40	100.41	19×10 ⁻³	0.9983	16.28	427.67	0.0846	0.9968	1.7065	0.995	0.1416
	50	99.85	18×10 ⁻³	0.9960	17.75	744.47	0.0913	0.9982	1.7284	0.997	0.1298
	60	101.59	17×10 ⁻³	0.9940	17.50	401.61	0.0818	0.9948	1.7105	0.999	0.1446
100	30	188.47	25×10 ⁻³	0.9946	26.66	297.98	0.0387	0.9961	1.6238	0.998	0.1705
	40	192.25	24×10 ⁻³	0.9988	27.23	353.65	0.0391	0.9987	1.6417	0.997	0.1647
	50	195.11	23×10 ⁻³	0.9954	29.74	442.24	0.0395	0.9967	1.6622	0.994	0.1590
	60	197.29	21×10 ⁻³	0.9990	32.32	712.14	0.0418	0.9989	1.6921	0.995	0.1462
150	30	265.76	28×10 ⁻³	0.9987	33.59	302.95	0.0263	0.9984	1.5714	0.997	0.1812
	40	269.83	27×10 ⁻³	0.9967	38.25	412.92	0.0268	0.9967	1.6016	0.999	0.1718
	50	278.59	26×10 ⁻³	0.9961	40.42	500.05	0.0267	0.9983	1.6260	0.998	0.1662
	60	281.20	24×10 ⁻³	0.9981	34.63	673.53	0.0288	0.9943	1.6406	0.997	0.1520
200	30	319.81	31×10 ⁻³	0.9975	34.36	200.22	0.0197	0.9982	1.4709	0.998	0.2079
	40	326.80	29×10 ⁻³	0.9969	38.74	273.80	0.0202	0.9972	1.5100	0.992	0.1946
	50	338.38	14×10 ⁻³	0.9973	39.64	267.73	0.0193	0.9969	1.5198	0.994	0.1973
	60	345.49	28×10 ⁻³	0.9989	44.37	382.72	0.0200	0.9981	1.5588	0.991	0.1830
250	30	364.90	31×10 ⁻³	0.9928	35.93	168.18	0.0163	0.9948	1.3953	0.992	0.2255
	40	377.59	32×10 ⁻³	0.9941	36.36	164.50	0.0156	0.9994	1.4028	0.991	0.2288
	50	391.93	20×10 ⁻³	0.9948	37.38	174.85	0.0152	0.9972	1.4219	0.992	0.2264
	60	397.03	31×10 ⁻³	0.9959	42.08	228.70	0.0156	0.9963	1.4589	0.991	0.2129

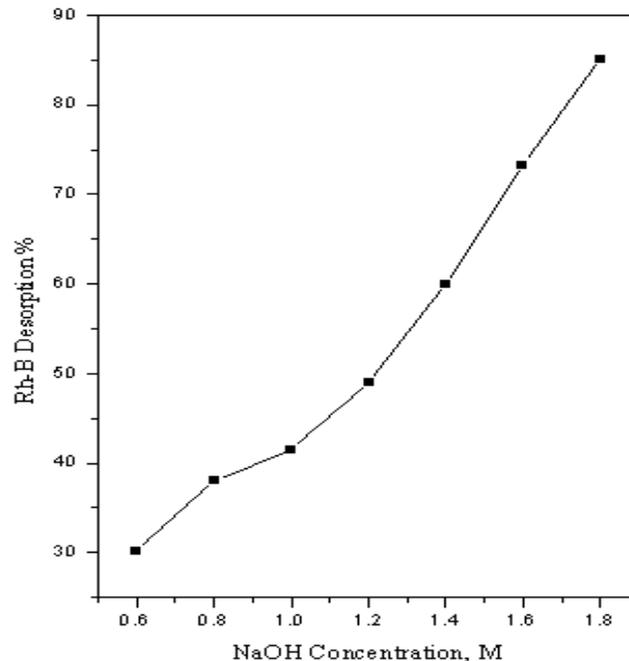


Figure-5: Effect of NaOH Concentration on Rhodamine-B desorption

Kinetic modeling in a batch system

In order to investigate the mechanism of adsorption kinetic models are generally used to test experimental data. Pseudo-first-order and pseudo-second-order equations can be used assuming that the measured concentrations are equal to surface concentrations, as discussed elsewhere [18]. The pseudo-first-order rate Lagergren model is:

$$\frac{dq}{dt} = k_{1,ads}(q_e - q) \quad (8)$$

Where, q (mg g^{-1}) is the amount of adsorbed heavy metals on the adsorbent at time t and $k_{1,ads}$ (min^{-1}) is the rate constant of first-order adsorption. The integrated form of Eq. (8) is:

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads}}{2.303} t \quad (9)$$

q_e the equilibrium sorption uptake, is extrapolated from the experimental data at time $t = \infty$. A straight line of $\log(q_e - q)$ versus t suggests the applicability of this kinetic model. q_e and $k_{1,ads}$ can be determined from the intercept and slope of the plot, respectively. The pseudo-second order kinetic model is expressed as:

$$\frac{dq}{dt} = k_{2,ads}(q_e - q)^2 \quad (10)$$

Where, $k_{2,ads}$ (g/mg min) is the rate constant of second-order adsorption. The integrated form of Eq. (10) is:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_{2,ads} t \quad (11)$$

Eq. (11) can be rearranged and linearized to obtain:

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{1}{q_e} t \quad (12)$$

The plot t/q versus t gives a straight line says second order kinetic model is applicable and q_e and $k_{2,ads}$ are determined from the slope and intercept of the plot, respectively. The high regression values shows the adsorption reaction is a pseudo-second-order one (table 6).

The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t/dt = \alpha \exp(-\beta q_t) \dots \dots \dots (13)$$

Where, α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation, as discussed by Chien and Clayton [19] assumed $\alpha\beta t \gg 1$ and by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq.(13) becomes:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \dots \dots \dots (14)$$

If Rh-B adsorption fits with the Elovich model, a plot of q_t vs $\ln(t)$ yields a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. The Elovich model parameters α , β , and correlation coefficient (γ) are summarized in table 6. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation coefficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase the pore or active site on the ACONC adsorbent.

Weber and Morris intra-particle diffusion model:-

Kinetic data was further analyzed using the Intraparticle diffusion model based on the theory proposed by Weber and Morris [20]. The amount of Rh-B adsorbed (q_t) at time ' t ' was plotted against the square root of time ($t^{1/2}$), according to eq.

$$Q_t = k_{id} t^{1/2} + C \quad (15)$$

Where, k_{id} is the Intraparticle diffusion rate constant and c is the intercept related to the thickness of the boundary layer. According to above equation a plot of qt versus $t^{1/2}$ gives a straight line from the origin says the adsorption mechanism follows the intra-particle diffusion process only. However, the data exhibit multilinear plots, says the process are governed by two or more steps, It is clear from that there are two separate zones: first linear portion (phase I) and second linear part (phase II). The first linear portion (Phase I) can be attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface, phase II may be attributed to very slow diffusion of the adsorbate from the surface site in to the inner pores. Thus initial portion of Rh-B adsorption by adsorbent may be governed by the initial intraparticle transport of Rh-B controlled by surface diffusion process and the later part controlled by pore diffusion. However, the intercept of the line fails to pass through the origin which may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of the straight lines from the origin reveals that the pore diffusion is not the sole rate – controlling.

Desorption studies

In order to assess the reusability of Rh-B-loaded Activated *Corchorus Olitorius L* biomass desorption experiments were carried out. The effect of strength of desorbing solution (NaOH) on the recovery of Rh-B is shown in Figure 5. It is evident from the above figure that when the strength of the desorbing solution increased from 0.5 to 2.0 M, Rh-B desorption percentage increased from 30% to 85%. Thus a significant amount of Rhodamine B is being desorbed, which shows that the ACONC biomass can be effectively reused after desorption.

CONCLUSION

The composite adsorbent exhibited effectiveness in the removal of Rh-B dye from aqueous solution. The removal efficiency was controlled by solution pH, adsorbent concentration, contact time and initial ion concentration. Adsorption data fitted well with the Langmuir and Freundlich models. However, Langmuir isotherm displayed a better fitting model than Freundlich isotherm because of the higher correlation coefficient that the former exhibited, thus, indicating to the applicability of monolayer coverage of the Langmuir dye on the surface of adsorbent. Using *Corchorus Olitorius L* to produce activated nano carbons potentially provides a less expensive raw material, a highly effective adsorbent as well as production of activated nano carbon processed from renewable resources instead of non-renewable ones.

ACKNOWLEDGEMENT

The authors sincerely thank the University Grants Commission, New Delhi for providing the fund from Major Research Project.

REFERENCES

- [1] Al Duri, B. McKay, G. El Geundi, M. Wahab S. & Abdul, M. Z. 1990. Three Resistance Transport Model for dye Adsorption onto Bagasse Pitch. J. Environ. Eng. Div., ASCE, 116, pp. 487.
- [2] Arivoli, S. Hema, M. Parthasarathy, S. & Manju, N. 2010. Adsorption dynamics of methylene blue by acid activated carbon. J. Chem. Pharm. Res., 2(5), pp. 626-641.
- [3] Hema, M. & Arivoli, S. 2009. Rhodamine B adsorption by activated carbon: Kinetic and equilibrium studies, Indian J. of Chem. Tech., 16(1), pp. 38-45.
- [4] Vijayakumaran, V. Arivoli, S. & Ramuthai, S. 2009. Adsorption of nickel ion by low cost carbon-kinetic, thermodynamic and equilibrium studies. E-Journal of Chemistry. 6(S1), pp. S347-S357.
- [5] Allen, S.J. McKay, G. & Khader, K.Y.H. 1989. Intraparticle Diffusions of Basic Dye During Adsorption onto Sphagnum Peat. Environ. Pollut., 56, pp. 39.
- [6] Alpert, N.L. Kesi, W.E. & Szymanaki, H.A. 1970. Theory and Practice of Infrared Spectroscopy. 2nd ed. Plenum: New York.
- [7] Crank, J. 1956. The Mathematics of Diffusion. Clarendon Press. Oxford.
- [8] El-Geundi, M.S. 1991. Colour Removal from Textile Effluents by Adsorption Technique. Wat. Res., 25, pp. 271.
- [9] Fornwalt, H.J. & Hutchins, R.A. 1966. Purifying Liquids with Activated Carbon. Chem. Eng. J., 73, pp. 179.
- [10] Freidal, R.A. & Queiser, J.A. 1956. Infrared Analysis of Bituminous Coal and Other Carbonaceous Materials. Anal. Chem., 28, pp. 22.
- [11] Gadsen, J.A. 1975. Infrared Spectra of Minerals and Related Inorganic Compounds Butterworths. London.
- [12] Freundlich, H. 1906. The dye adsorption isotherms (Adsorption in Solution). Z. Phys. Chem., 57, pp. 385-470.

- [13] Langmuir, I.1918. The adsorption of gases plane surfaces of glass, mica and platinum. J. Am.Soc.,579, pp. 1361-1403.
- [14] Gupta, G.S. Prasad, G. & Singh, V.N.1988. Removal of Chrome Dye from Carpet Effluents using Coal II (Rate process). Environ. Technol. Lett.,9, pp. 1413.
- [15] Khan, A.A, &Singh, R.P.1987. Adsorption thermodynamics of carbofuran on Sn (IV) arsenosilicate in H⁺, Na⁺ and Ca²⁺ forms. Colloid & Surfaces. 24, pp. 33-42
- [16] Weber, T.W. &Chakravorti, R.K.1974. Pore and Solid diffusion models for fixed bed adsorbers. J. Am. Inst. Chem. Eng.,20,pp. 228.
- [17] McKay, G. Blair, H.S. & Gardner, J.R. 1982. Adsorption of dyes on chitin. I. Equilibrium Studies. J. Appl.Polym. Sci.,27, pp. 3043-3057.
- [18] Arivoli, S.Venkataraman, B.R. Rajachandrasekar, T.&Hema, M.2008. Res. J. Chem. Environ., 17,pp. 70-78.
- [19] Chien, S. H. & Clayton, W.R.1980. Application of Elovich Equation to the kinetics of Phosphate release and sorption on soil. Soil Sci. Sco. Am. J., 44, pp. 265-268.
- [20] Weber, W. J. & Morris, J.C.1964. Kinetics of adsorption on Carbon from solution. J. Sanitary Eng. Div.,90, pp. 79.