



KINETICS, THERMODYNAMICS AND ISOTHERM ANALYSIS ON THE REMOVAL OF RHODAMINE B DYE ONTO PONC

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ABSTRACT

Application of *Posidonia Oceanica* for the removal of a Cationic dye, Rhodamine B, from aqueous solutions has been investigated. The experiments were carried out in batch mode. Effect of the parameters such as pH, initial dye concentration and temperature on the removal of the dye was studied. Equilibrium was achieved in 60 min. Maximum adsorption of dye was achieved at pH 6.2. Removal percentage was found to be dependent on the initial concentration of dye solution and maximum removal was found to be 88% at 25 mg/L of Rhodamine B. The removal increases from 75% to 88% when the initial concentration of dye solution decreases from 125 mg/L to 50 mg/L. The equilibrium adsorption data were analyzed by Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The (Langmuir) adsorption capacity of the adsorbent is found to be 280 mg/g at 303 K. Kinetic modeling of the process of removal was carried out and the process of removal was found to follow a pseudo second order model. The thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined and the negative values of ΔG indicated that the process of removal was spontaneous at all values of temperatures. Further, the values of ΔH indicated the endothermic nature of the process of removal.


Keywords: Activated *Posidonia Oceanica* Nano Carbon (PONC); Rhodamine-B dye; Adsorption isotherm; Kinetics; Equilibrium models.

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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 [1]. Several physical and chemical

methods have been developed for the removal of organic dyes from industrial effluents [2]. Physical methods, mainly adsorption on various supports were recognized to be a promising and effective process to remove dyes from industrial waste waters completely [3,4]. 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 (600-900°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

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simultaneously in presence of dehydrating agent such as H_3PO_4 , HNO_3 , KOH , $NaOH$, H_2O_2 , H_2SO_4 . Chemically activated carbon has higher yield, more surface area and better development of porous structure than that obtained by physical activation [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. *Posidonia Oceanica* is the most ancient plant of India. It is found throughout 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 Shell of a *Posidonia Oceanica* 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 *Posidonia Oceanica* as an adsorbent.

MATERIALS & 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 *Posidonia Oceanica* used in the present investigations was collected from a nearby Thiruvavur area. The leave 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 Shell was carried out by adding w/v ratio $Con.H_2SO_4$ 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.

Figure 1. *Posidonia Oceanica*



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 *Posidonia Oceanica* Nano Carbon. For Adsorption Isotherms, dye solution of different concentrations (25-125 mg/L) and at different temperatures (30- 60 °C) with known pH and known amount of adsorbent (25 mg/L) were agitated at 120 rpm 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 554 nm. All experiments were carried out at normal pH for RH-B. Effect of pH on dye removal was studied over a pH range of 2.0-9.0 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 (25–125 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

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

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

Table 1. Characteristics of the Adsorbent

Properties	PONC
Particle size(nm)	29.00
Density (g/cc)	0.211
Moisture content (%)	0.165
Loss in ignition (%)	0.009
pH of aqueous solution	6.200

Effect of 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 PONC adsorbent was investigated as a function of contact time and the results were shown in fig 1. The figure shows that the uptake rate was initially rapid with 50% of the adsorption was complete with in 30 min, Equilibrium was achieved with in 50 min 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.

Effect of adsorbent dosage

The adsorption of the RH-B dye on PONC was studied by varying the adsorbent dose (25–125 mg/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased with increases in the PONC dose, which is attributed to increased carbon surface area and the availability of more adsorption sites [6, 7]. Hence, all studies were carried out with 0.025g of adsorbent/50 ml of the varying adsorbate solutions. 25, 50, 75, 100 and 125 mg/L. 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 PONC. This reveals that the direct and equilibrium capacities of RH-B are functions of the activated PONC dosage.

Effect of Initial pH

Previous research [8] 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 2-9 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. At lower pH values ($pH <$

pH_{zpc}) the surface charge of the surface of PONC 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 PONC lead to a decrease in the uptake of dye molecules. In contrast at higher pH values ($pH > pH_{zpc}$) the surface of PONC 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 Posidonia Oceanica. As a result, the initial pH value was optimized as 6.2 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 PONC, 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 [9].

Adsorption Models

Adsorption isotherm [10] describes the relation between the amount or concentration of adsorbate that accumulates on the adsorbent and the equilibrium concentration of the dissolved adsorbate. Equilibrium studies were carried out by agitating a series of beakers containing 100 mL of Rhodamine B (RH-B) dye solutions of initial concentration 25 mg/L with 0.025 g of activated nano carbon at 30 °C with a constant agitation. Agitation was provided for 1.0 h, which is more than sufficient time to reach equilibrium.

Freundlich adsorption isotherm

The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption. The

adsorption isotherm is expressed by the following equation

$$q_e = K_F C_e^{1/n_F} \dots\dots\dots (3)$$

Which, can be linearized as

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \dots\dots\dots (4)$$

Where, q_e is the amount of RH-B dye adsorbed at equilibrium (mg/g) and C_e is the concentration of RH-B dye in the aqueous phase at equilibrium (ppm). K_F (L/g) and $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ Vs $\ln C_e$ plot and the model parameters are shown in Table 3. The magnitude of K_F showed that PONC had a high capacity for RH-B dye adsorption from the aqueous solutions studied. The Freundlich exponent, n_F , should have values in the range of 1 and 10 (i.e., $1/n_F < 1$) to be considered as favourable adsorption [23]. A $1/n_F$ value of less than 1 indicated that RH-B dye is favorably adsorbed by PONC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm in a linear form can be represented as [11]

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \dots\dots\dots (5)$$

Where q_e is the amount of RH-B dye adsorbed at equilibrium (mg/g), C_e is the concentration of RH-B in the aqueous phase at equilibrium (ppm), q_m is the maximum RH-B dye uptake (mg/g), and K_L is the Langmuir constant related to adsorption capacity and the energy of adsorption (g/mg).

A linear plot of C_e/q_e Vs C_e was employed to determine the value of q_m and K_L , and the data so obtained were also presented in Table 3. The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreased with an increase in the temperature. A high K_L value indicates a high adsorption affinity. The Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \dots\dots\dots (6)$$

Where, C_0 is the initial RH-B dye concentration (ppm). Four scenarios can be distinguished:

The sorption isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, The isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor (R_L) for RH-B dye removal were calculated at different concentrations and temperatures. As shown in Table 4, at all concentrations and temperatures tested the values of R_L for RH-B dye adsorptions on the PONC were less than 1 and greater than zero, indicating favorable adsorption.

The Langmuir isotherm showed a better fit to the adsorption data than the Freundlich isotherm. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the PONC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

Temkin adsorption isotherm:

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions [12] The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \dots\dots\dots (7)$$

Which, can be represented in the following linear form

$$\dots\dots\dots q_e = \left(\frac{RT}{b_T}\right) \ln K_T + \frac{RT}{b_T} \ln C_e \dots\dots\dots (8)$$

Where, K_T (L/g) is the Temkin isotherm constant, b_T (J/mol) is a constant related to heat of sorption, R is the ideal gas constant (8.314 J/mol K), and T is absolute temperature (K). A plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_T and b_T from the slope and intercept. The model parameters are listed in Table 3. The Temkin isotherm appears to provide a good fit to the RH-B dye adsorption data.

The adsorption energy in the Temkin model, b_T , is positive for RH-B dye adsorption from the aqueous solution, which indicates that the adsorption is endothermic. The experimental equilibrium curve is close to that predicted by Temkin model. Consequently, the adsorption isotherm of RH-B dye on PONC can be described reasonably well by the Temkin isotherm.

Hurkins-Jura adsorption isotherm

The Hurkins-Jura adsorption isotherm can be expressed as [13]

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} \dots\dots\dots(9)$$

This can rearranged as follows:

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e \dots\dots\dots(10)$$

Where, A_H (g^2/L) and B_H (mg^2/L) are two parameters characterizing the sorption equilibrium.

The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. The Harkins–Jura isotherm parameters are obtained from the plots of $1/q_e^2$ versus $\log C_e$ enables the determination of model parameters A_H and B_H from the slope and intercept.

Halsay adsorption isotherm

The Halsay adsorption isotherm can be given as [14]

$$q_e = \exp\left(\frac{\ln K_{Ha} - \ln C_e}{n_{Ha}}\right) \dots\dots\dots(11)$$

And, a linear form of the isotherm can be expressed as follows:

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}} \dots\dots\dots(12)$$

Where, K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants.

A plot of $\ln q_e$ Vs $\ln C_e$ enables the determination of n_{Ha} and K_{Ha} from the slope and intercept. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of adsorbent. The experimental data and the model predictions based on the non-linear form of the Halsay models. The model parameters are listed in Table 3. This result also shows that the adsorption of RH-B dye on PONC was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of RH-B dye on PONC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

Redlich-Peterson adsorption isotherm

The Redlich-Peterson adsorption isotherm contains three parameters and incorporates the features of Langmuir and Freundlich isotherms into a single equation. The general isotherm equation can be described as follows [15]

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \dots\dots\dots(13)$$

The linear form of the isotherm can be expressed as follows:

$$\ln \frac{C_e}{q_e} = g \ln C_e - \ln K_R \dots\dots\dots(14)$$

Where, K_R (L/g) and a_R (L/mg) are the Redlich-Peterson isotherm constants and g is the exponent between 0 and 1. There are two limiting cases: Langmuir form for $g = 1$ and Henry’s law for $g = 0$.

A plot of $\ln C_e/q_e$ versus $\ln C_e$ enables the determination of isotherm constants g and K_R from the slope and intercept. The values of K_R , presented in Table 3, indicate that the adsorption capacity of the PONC decreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

Dubinin-Radushkevich adsorption isotherm

The Dubinin-Radushkevich adsorption isotherm is another isotherm equation [32]. It is assumed that the characteristic of the sorption curve is related to the porosity of the adsorbent. The linear form of the isotherm can be expressed as follows [16]

$$\ln q_e = \ln Q_D - B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \dots\dots\dots(15)$$

Where, Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol^2/kJ^2). A plot of $\ln q_e$ Vs $RT \ln(1+1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept.

Jovanovic adsorption isotherm

The model of an adsorption surface considered by Jovanovic [17] is essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship [29]:

$$q_e = q_{max} \left(1 - e^{-K_J C_e} \right) \dots\dots\dots(16)$$

The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln q_{max} - K_J C_e \dots\dots\dots(17)$$

Where, K_J (L/g) is a parameter. q_{max} (mg/g) is the maximum RH-B dye uptake.

The q_{max} is obtained from a plot of $\ln q_e$ and C_e . Their related parameters are listed in Table 3.

By comparing the values of the error functions, it was found the Langmuir and Temkin models are best to fit the RH-B adsorption on the PONC. Both models show a high degree of correlation. This is clearly confirming the good fit of

Langmuir and Temkin models with the experimental data for removal of RH-B dye from the solution.

The Brunauer–Emmett–Teller (BET) isotherm model

Brunauer-Emmett-Teller (BET) [18] isotherm is a theoretical equation, most widely applied in the gas–solid equilibrium systems. It was developed to derive multilayer adsorption systems with relative concentration ranges from 25 to 125 mg/L corresponding to a monolayer coverage lying between 25 and 75 mg/L. Its extinction model related to liquid–solid interface is exhibited as:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)(C_e / C_s)]} \dots\dots\dots(18)$$

Where, CBET, Cs, qs and qe are the BET adsorption isotherm (L/mg), adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. As CBET and CBET (Ce/Cs) is much greater than 1,

In the linear form as used is represented as

$$\frac{C_e}{q(C_s - C_e)} = \frac{1}{q_s C_{BET}} + \left(\frac{C_{BET} - 1}{q_s C_{BET}} \right) \left(\frac{C_e}{C_s} \right) \dots\dots\dots(19)$$

Where, Ce is equilibrium Concentration (mg/l), Cs is adsorbate monolayer saturation concentration (mg/l) and CBET is BET adsorption relating to the energy of surface interaction (l/mg) the BET model.

Kinetic parameters

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Dye adsorption on solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of dye molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the adsorption kinetics of the dye, the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion models were applied. Each of these models and their linear modes of them equations presented in below. Where, qe and qt refer to the amount of (RH-B) dye adsorbed (mg/g) at equilibrium and at any time, t (min), respectively and k1 (1/min), k2 (g/mg.min) are the equilibrium rate constants of pseudo-first order and pseudo-second order models, respectively.

Pseudo-first order model is a simple kinetic model, which was proposed by Lagergren during 1898 and is used for estimation of the surface adsorption reaction rate. The values of ln (qe - qt) were linearly correlated with t. The plot of ln (qe - qt) vs. t should give a linear relationship from which the values of k1 were determined from the slope of the plot. In many cases, the first-order equation of Lagergren does not fit well with the entire range of

contact time and is generally applicable over the initial stage of the adsorption processes.

In the pseudo-second order model [19], the slope and intercept of the t/qt Vs t plot were used to calculate the second-order rate constant, k2. The values of equilibrium rate constant (k2) are presented in Table 6. According to Table 6, the value of R² (0.999) related to the pseudo-second order model revealed that (RH-B) dye adsorption followed this model, Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the Mechanism of diffusion of dye into the adsorbent pores.

The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t / dt = \alpha \exp (-\beta q_t) \dots\dots\dots(20)$$

Where; α is the initial adsorption rate (mg g⁻¹ min⁻¹) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation, Chien and Clayton [20] assumed αβt >> t and by applying boundary conditions qt = 0 at t= 0 and qt = qt at t = t Eq. (20) becomes:

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln t \dots\dots\dots (21)$$

If RH-B adsorption fits with the Elovich model, a plot of qt Vs ln(t) yields a linear relationship with a slope of (1/β) and an intercept of (1/β)ln (αβ). 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 PONC 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 (qt) at time ‘t’ was plotted against the square root of time (t^{1/2}), according to eq.

$$Qt = k_{id} t^{1/2} + C \dots\dots\dots(22)$$

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 multi linear 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.

Thermodynamic parameters

Thermodynamic parameters [15] were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. Enthalpy change (ΔH), and entropy change (ΔS) may be determined from Van't Hoff equation:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (23)$$

By plotting $\ln K$ as ordinate and $1/T$ as abscissa, we will get ΔS , ΔH and by using the following equation. We can get the value of have ΔS , ΔH .

And by this equation, get the value of ΔG .

$$\Delta G = \Delta H - T \Delta S \dots\dots\dots (24)$$

Where, ΔG is the free energy change (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), K is the thermodynamic equilibrium constant and T is the absolute temperature (K).

$$\Delta G = \Delta H - T \Delta S = -RT \ln K_c \dots\dots\dots (25)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (26)$$

$$2.30 \log \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (27)$$

$$\log \frac{q_e}{C_e} = \frac{\Delta S}{R \times 2.303} - \frac{\Delta H}{RT \times 2.303} \dots\dots (28)$$

The values of ΔS , ΔH , ΔG was obtained from a plot of $\log (q_e/C_e)$ vs. $1/T$.

Heat of reaction (ΔH) for physical adsorption is reported to be 4.1 to 30 kJ/ mol in literature. The value of ΔH range from 8.89 to 11.543 kJ/mol from Table-5 which indicate that the nature of adsorption of Rhodamine B (RH-B) dye on PONC is physical adsorption. The negative value of ΔG indicate endothermic and spontaneous process of

adsorption of Rhodamine B (RH-B) dye on PONC respectively.

In order to support that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were calculated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows:

$$\theta = \left[1 - \frac{C_e}{C_i} \right] \dots\dots\dots (29)$$

$$S^* = (1 - \theta)_e \frac{-E_a}{RT} \dots\dots\dots (30)$$

The sticking probability, S^* , is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition $0 < S^* < 1$ and is dependent on the temperature of the system. The values of E_a and S^* can be calculated from slope and intercept of the plot of $\ln(1-\theta)$ versus $1/T$ respectively and are listed in Table 5.

From Table 5 it is clear that the reaction is spontaneous in nature as ΔG values are negative at all the temperature studied. Again positive ΔH value confirms that the sorption is endothermic in nature. The positive value of ΔS reflects the affinities of the adsorbents for the RH-B dye. The result as shown in Table 5 indicate that the probability of the RH-B dye to stick on surface of biomass is very high as $S^* \ll 1$, these values confirm that, the sorption process is physisorption.

Desorption studies

In order to assess the reusability of RH-B-loaded Activated *Posidonia Oceanica* 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 PONC biomass can be effectively reused after desorption [20].

CONCLUSION

On the basis of the above studies, the following can be concluded:

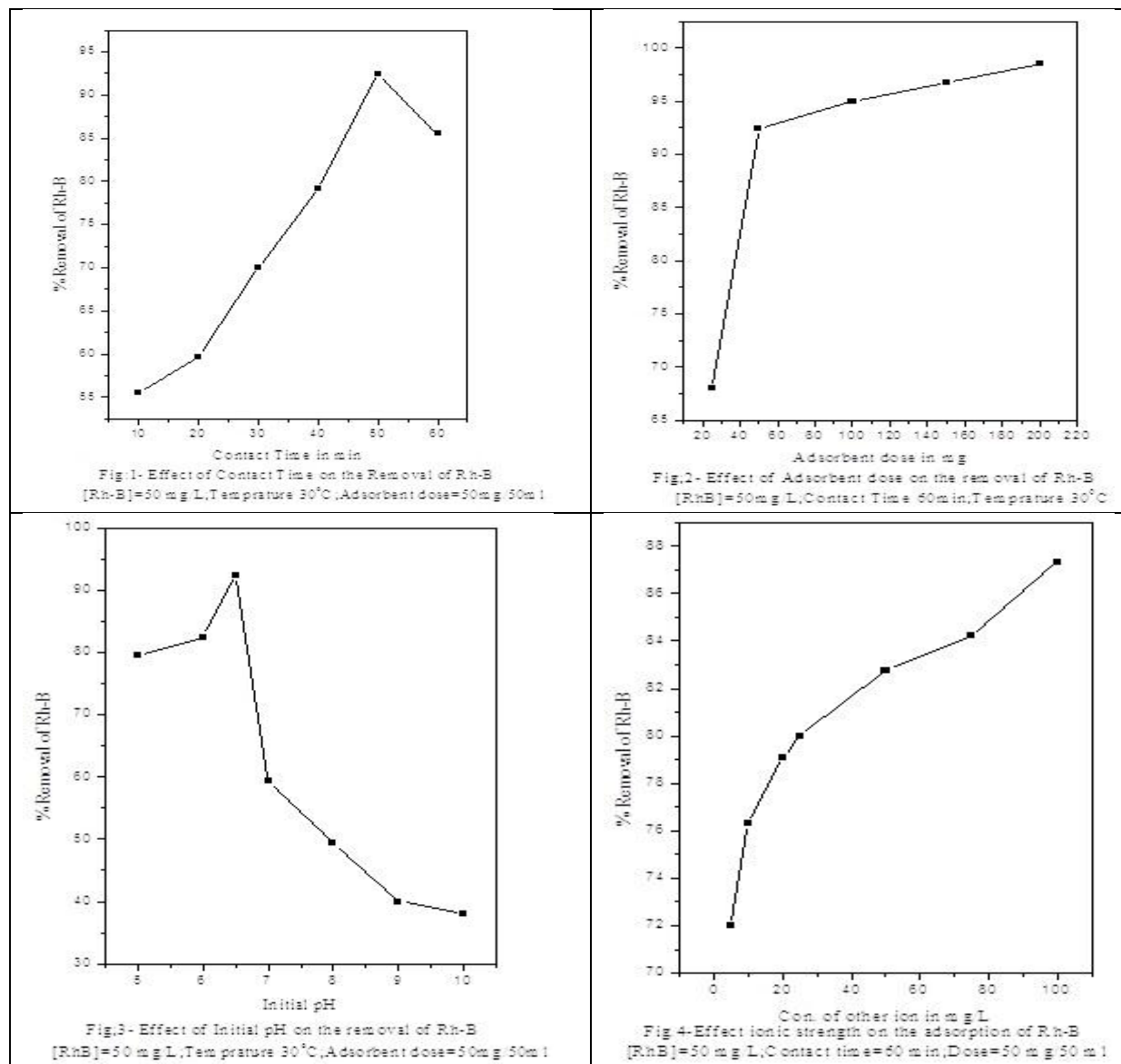
- i. Characterization of Activated *Posidonia Oceanica* was carried out which revealed that the surface of the adsorbent was rough and suitable for adsorption.
- ii. *Posidonia Oceanica* Nano Carbon has shown a potential to remove Rhodamine B from aqueous solution.

iii. Initial concentration of the dye plays an important role in the removal process.

iv. Kinetics of the process removal was studied and the values of rate constants were determined. The dye removal was found to be governed by film diffusion mechanism where external transport of the adsorbate over surface of the adsorbent is greater than internal transport which was confirmed by the Boyd plot and the process of removal was found to follow second order kinetics.

v. Thermodynamic parameters were calculated for the removal of dye and their values indicated that the process of removal was spontaneous and endothermic.

vi. The data were found to best fitted in Langmuir and BET isotherm model. It can therefore be concluded that *Posidonia Oceanica* offers promise as an economically viable alternative for sequestering of the dye from the aqueous solution. The work can be extended for the removal of dyes from effluents as well.



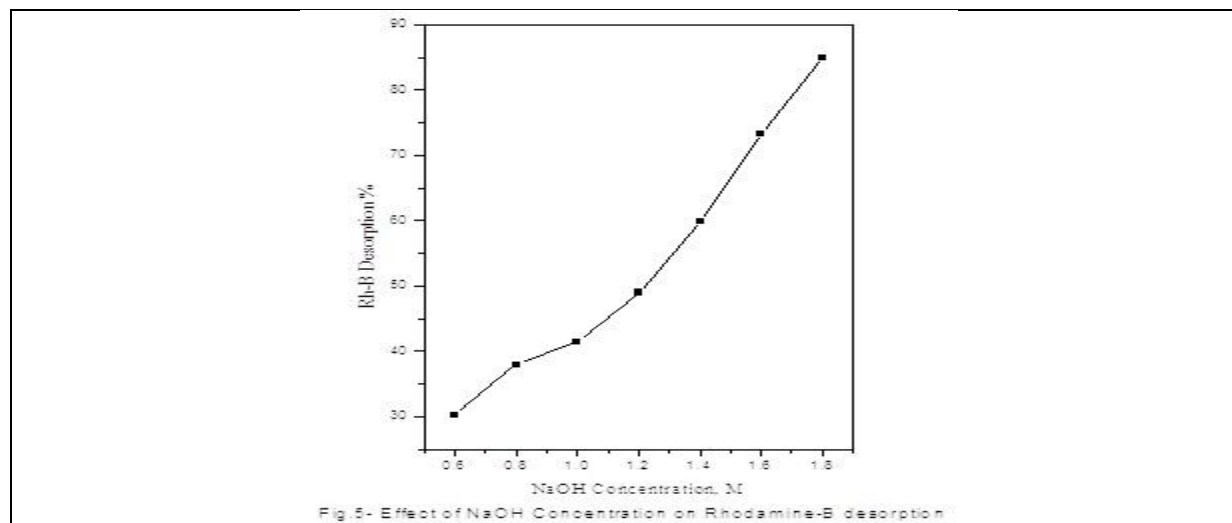


Fig. 5- Effect of NaOH Concentration on Rhodamine-B desorption

Kinetic Models and Their Linear Forms			
Model	Nonlinear Form	Linear Form	Number of Equation
Pseudo-first-order	$dq_t/dt = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	(18)
Pseudo-second-order	$dq_t/dt = k_2(q_e - q_t)^2$	$t/q_t = 1/k_2 q_e^2 + (1/q_e)t$	(19)

Table 2. Equilibrium Parameters for the Adsorption of RH-B onto PONC

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
25	3.004	1.802	1.203	1.142	43.99	46.40	47.59	47.72	87.99	92.79	95.19	95.43
50	6.608	6.010	5.432	4.207	86.78	87.98	89.14	91.59	86.78	87.98	89.14	91.59
75	14.47	13.10	11.41	10.58	121.1	123.8	127.2	128.8	80.71	82.53	84.78	85.90
100	21.08	19.27	18.28	17.15	157.8	161.5	163.4	165.7	78.92	80.73	81.72	82.85
125	31.24	30.16	29.49	27.74	187.5	189.7	191.0	194.5	75.01	75.88	76.41	77.81

Table 3. Isotherm Parameter for the Adsorption of RH-B onto PONC

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f (mg/g) (L/mg) ^{1/n}	24.480	34.830	43.382	46.285
	n	1.6531	1.9825	2.2572	2.2691
Langmuir	Q _m (mg/g)	280.19	245.06	230.61	229.91
	b (L/mg)	0.0612	0.0999	0.1383	0.1629
Temkin	b _T (J/mol)	59.843	50.498	44.769	45.487
	K _T (L/mg)	0.540	1.157	1.615	1.744
Hurkins-Jura	A _H (g ² /L)	-2222.7	-2804.1	-3286.7	-3414.9
	B _H (mg ² /L)	-1.4049	-1.3899	-1.3771	-1.3421
Halsay	K _{Ha} (mg/L)	197.6	1139.9	4963.1	6011.6
	n _{Ha}	1.6531	1.9825	2.2572	2.2691
Radlich-Peterson	g	0.3951	0.4956	0.5570	0.5593
	K _R (L/g)	0.0408	0.0287	0.0231	0.0216
Dubinin-Radushkevich	q _s (mg/g)	150.03	143.45	142.44	147.20
	K _D × 10 ⁻⁴ mol ² kJ ⁻²	1.6188	1.6005	1.5928	1.5992
Jovanovic	K _J (L/g)	0.0463	0.0459	0.0450	0.0469
	q _{max} (mg/g)	52.485	57.235	61.392	63.677
BET	C _{BET} (L/mg)	8.465	15.320	23.874	28.088
	q _S (mg/g)	0.1181	0.0653	0.0419	0.0356

Table 4. Dimensionless Separation Factor (R_L) for the Adsorption of RH-B onto PONC

(C_i)	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.3951	0.2860	0.2244	0.1972
50	0.2462	0.1668	0.1264	0.1094
75	0.1788	0.1178	0.0879	0.0757
100	0.1404	0.0910	0.0674	0.0578
125	0.1155	0.0742	0.0547	0.0468

Table 5. Thermodynamic Parameter for the Adsorption of RH-B onto PONC

(C_0)	ΔG°				ΔH°	ΔS°	E_a	S^*
	30°C	40°C	50°C	60°C				
25	-5015.6	-6648.9	-8015.4	-8415.8	30.248	117.21	27963.2	0.0000017
50	-4740.9	-5179.8	-5652.0	-6609.8	13.581	60.145	12123.4	0.0011
75	-3605.6	-4041.4	-4612.3	-5002.6	10.8437	47.670	9046.67	0.0053
100	-3326.0	-3727.1	-4020.8	-4360.6	6.9701	34.053	5641.86	0.0223
125	-2768.7	-2981.9	-3155.9	-3473.4	4.1396	22.750	3162.62	0.0716

Table 6. The Kinetic Parameters for Adsorption for the Adsorption of RH-B onto PONC

C_0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
25	30	50.28	0.0019	0.9904	4.92	235.3	0.1195	0.9896	0.2241	0.9965	1.5364
	40	49.40	0.0043	0.9896	10.37	758.0	0.1992	0.9916	0.1182	0.9892	1.7516
	50	49.42	0.0071	0.9924	17.25	723.6	0.2985	0.9956	0.0744	0.9911	1.8424
	60	49.44	0.0075	0.9935	18.36	153.2	0.3145	0.9926	0.0702	0.9901	1.8511
50	30	94.55	0.0015	0.9957	13.41	224.4	0.0834	0.9960	0.1559	0.9948	1.6487
	40	95.20	0.0017	0.9924	15.06	344.3	0.0873	0.9906	0.1455	0.9901	1.6756
	50	96.11	0.0019	0.9950	17.42	572.7	0.0915	0.9926	0.1352	0.9891	1.7046
	60	97.36	0.0021	0.9967	20.00	145.5	0.1010	0.9896	0.1184	0.9911	1.7438
75	30	128.2	0.0016	0.9907	26.09	358.6	0.0831	0.9906	0.1083	0.9951	1.7026
	40	132.3	0.0017	0.9898	30.33	274.4	0.0764	0.9967	0.1140	0.9891	1.7133
	50	137.1	0.0015	0.9890	27.64	104.9	0.0656	0.9952	0.1309	0.9911	1.6954
	60	136.3	0.0021	0.9892	39.35	486.0	0.0772	0.9968	0.1081	0.9891	1.7455
100	30	168.4	0.0016	0.9911	44.51	252.3	0.0567	0.9942	0.1208	0.9932	1.6886
	40	171.9	0.0015	0.9920	43.56	251.7	0.0556	0.9901	0.1210	0.9901	1.6957
	50	173.5	0.0016	0.9941	47.35	351.3	0.0570	0.9931	0.1161	0.9956	1.7105
	60	175.8	0.0016	0.9952	48.61	402.2	0.0570	0.9963	0.1143	0.9912	1.7197
125	30	199.1	0.0009	0.9939	36.67	227.6	0.0484	0.9909	0.1217	0.9914	1.6453
	40	201.6	0.0009	0.9960	36.92	224.2	0.0476	0.9969	0.1222	0.9901	1.6497
	50	202.1	0.0010	0.9907	39.78	382.5	0.0504	0.9956	0.1139	0.9911	1.6680
	60	206.2	0.0008	0.994	38.03	253.9	0.0472	0.9926	0.1204	0.9943	1.6629

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