

**ICEWEST-2015 [05th - 06th Feb 2015]****International Conference on Energy, Water and
Environmental Science & Technology****PG and Research Department of Chemistry, Presidency College (Autonomous),
Chennai-600 005, India****Removal of Rhodamine B from aqueous solution by activated
carbon prepared from the natural plant Typha latifolia by
adsorption: Kinetic and Isotherm Studies****H. Jayasantha kumari^{1,2}, P. Krishnamoorthy^{3*}, T.K. Arumugam³****¹Research and Development Centre, Bharathiar University, Coimbatore 641 046, India,****²Department of Chemistry, Priyadarshini Engineering College, Vaniyambadi, India.****^{3*}Department of Chemistry, Dr. Ambedkar Govt. Arts College,
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Abstract: The Rhodamine-B (RhB) is a well-known water soluble xanthene organic dye, which is widely used in varying industries resulting in the dye effluents with various concentrations. The RhB in water even at low concentrations interferes with penetration of sunlight into water and the gas solubility in water, retards photosynthesis, inhibits the growth of aquatic biota and is a suspected carcinogen. To remove the toxic dyes like RhB a low-cost abundant adsorbents was investigated. The removal of colorant from effluent is one of the major environmental problem. Typha latifolia stem and leaves are used to prepare the activated carbon which was used as a novel adsorbent. The influence of pH, adsorbent dose and contact time, adsorbent nature and concentration on the selectivity and sensitivity of the removal process was investigated. The kinetics of adsorption process was studied by Lagergren's pseudo-first order and pseudo-second order kinetics and the adsorption process depends on both time and concentration. The feasibility of the sorption was studied using Freundlich and Langmuir isotherms including linear regression methods. Various thermodynamic parameters such as the standard Gibbs free energy (ΔG°), standard entropy (ΔS°), and standard enthalpy (ΔH°) were calculated. The activated charcoal adsorbent material was characterized by using Fourier Transform Infrared Spectroscopy (FTIR). This readily available low-cost adsorbent is efficient in the uptake of removing the RhB dye in aqueous solution, thus, it could be an excellent alternative for the removal of dyes and organic matter from water and wastewater.

Key Words: Typha latifolia carbon, dye Rhodamine B, adsorption, kinetics, thermodynamics.

Introduction

Organic dyes are very widely used in industries such as textiles, paper, plastics, leather, food and cosmetics to give colour products. Most of these dyes cause serious environmental and health problems such as mutagenic and carcinogenic effects¹, due to their chemical stability and difficulty in decomposition². Untreated

disposal of this colored water into water bodies lead to serious effects on aquatic life or human beings, discharge of such effluents is a problem in terms of toxicological and environmental reasons³. Various treatment processes have been used to remove the pollutant from effluents. Among all the approaches, adsorption is one of the most common methods which are popularly considered as an effective and economic viable method for treatment of effluents⁴. Further, adsorption is superior to other wastewater treatment method in terms of its low cost, flexibility and design simplicity and inactive towards toxic pollutants⁵.

Activated carbon is a versatile adsorbent used widely for adsorption process, however, it has limitation because of its high cost and need for regeneration⁶. Due to expensiveness of activated carbon many researchers have been involved in the work of production of activated carbon from economical and viable materials that are available in nature. Certain natural materials, biosorbents and waste from industrial and agricultural operations represent potentially suitable alternative adsorbents. In recent years, volumes of literature available that illustrates the finding of inexpensive and effective alternatives to activated carbon like saw dust⁷, coconut coir⁸, chitin⁹, lemon peel¹⁰, banana pith¹¹, silica-zirconia mixed oxide¹², neem leaf¹³, rich husk¹⁴, orange waste¹⁵.

Although there are a number of reports on the adsorption of organic dye onto different types of adsorbents, it is necessary to investigate any potential local resources that would possess the required adsorption characteristics. Therefore, there is a need to produce a low cost, easily and abundantly available adsorbent which can be employed in waste water environment to remove dye organic and investigate adsorption properties¹⁶.

In this present work, a low cost material, *Typha latifolia*, a variety of broad leaf cattail type bioremediator, stem and leaves (TLAC) has been used for the development of activated carbon. The process used for activation of carbon is simple and economically viable. The work presents data and the process of removal of Rhodamine-B (RhB) an organic dye has been optimized using various parameters such as TLAC dosage, initial pH and temperature by carrying batch experiments. The adsorption kinetics, isotherms and thermodynamics studies have been performed to understand the processes of removal of selective dye (RhB) on TLAC. The surface functional group characterization of the adsorbent material was done using Fourier Transform Infrared Spectroscopy (FTIR).

Materials and methods

Preparation of activated carbon

Typha latifolia activated Carbon (TLAC) was prepared from *Typha latifolia* stem and leaves. It was collected in Dr.Ambedkar Government Arts College, Chennai, premises and the stem was dried without sunlight for 10 days and carbonized with 1:1 sulfuric acid. Carbon was washed with distilled water to attain neutral pH and dried in hot air oven at 423 K for 24 h then kept in a muffle furnace at 773 K for complete carbonization. Carbon was powdered in a ball mill to get the desired size of an activated carbon.

Preparation of dye solution

Rhodamine-B [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride its molecular formula $C_{28}H_{31}ClN_2O_3$; Rhodamine-B obtained from Merck, India limited (analytical grade (assay 99.8%)) was dissolved in deionized water to prepare 100 mg/l as stock solution, while the working solution was prepared by diluting the solution. For spectrophotometric measurements a number of standard solutions were prepared in the concentration range of 0.1-100 mg l⁻¹ by successive dilutions in order to obtain the calibration curve for the determination of solution concentration.

Sorption studies

Batch adsorption studies of RhB onto TLAC were determined by various parameters such as pH, metal concentration, adsorbent dose, contact time and temperature. The optimum concentration of dye solution was evaluated using 4 to 16 mg L⁻¹ with 4 mg L⁻¹ variation using 40 mL of dye solution. For the determination of the effect of pH of the sorption process, the pH values were adjusted from 2 to 10 using 0.1 M NaOH and 0.1 M HCl with a Elico pH meter. The adsorbent dosage was varied from 0.1 g to 1 g with 0.1 g variation. The effect of temperature of sorption process was estimated by using various temperatures as 303 K, 313 K, 323 K and 333 K. The contact time of the process was predicted by varying the contact time as 10–80 min with 10 min variation. The RhB concentration of supernatant liquids was determined by using UV–Vis Spectrophotometer

(λ max: 550 nm) model Elico Double Beam SL191 UV-Spectrophotometer. The percentage removal of CV was calculated using the following relationship

$$\% \text{ CV removal} = (C_o - C_t) / C_o \times 100 \quad \text{----- [1]}$$

Where C_o (mg/l) and C_t (mg/l) are the dye concentration at initial and at time respectively.

Isotherm and kinetic studies

The isotherm equations used in this study are Freundlich and Langmuir isotherm equations of linear regression methods. In Langmuir isotherm various forms of linearized equations were examined. The amount of sorption at equilibrium q_e (mg g^{-1}), calculated by the following equation,

$$q_e = (C_o - C_e) \times V / W \quad \text{----- [2]}$$

where, C_o and C_e (mg L^{-1}) are the liquid phase concentration of RhB at initial and equilibrium respectively. Kinetic study helps to predict the mechanisms involved during the sorption process. In order to obtain kinetic data of the adsorption process Lagergren's pseudo-first order and pseudo-second order kinetic equations were used.

Characterization of the adsorbent

The *Typha latifolia* stem carbon was characterized by using FTIR Spectroscopy. The FTIR provides the information about the type of functional groups present on the surface of the adsorbent material. FTIR shows that changes occur on the surface of the adsorbent before and after adsorption of the adsorbate molecule.

Results and discussion

FTIR studies

FTIR studies are used for prediction of different types of functional groups present in the adsorbent material. The FTIR spectrum of carbon is presented in Fig.1. The carbon spectrum shows the peaks in the positions of 3732 cm^{-1} , 3452 cm^{-1} , 2534 cm^{-1} , 2018 cm^{-1} , 1707 cm^{-1} , 1618 cm^{-1} , 1359 cm^{-1} and 1146 cm^{-1} . The peak position of 3452 cm^{-1} indicates that the presence of stretching vibration of the OH group involves in the intermolecular or intra-molecular hydrogen bonding or moisture present either in carbon or KBr. The peak positions at 2018 cm^{-1} , 1618 cm^{-1} , 1193 cm^{-1} and 1035 cm^{-1} shows that the presence of alkyl group or due to the presence of tannin, C-C bond in aromatic conjugation, C-N peptide bond and S, O interaction respectively¹⁷.

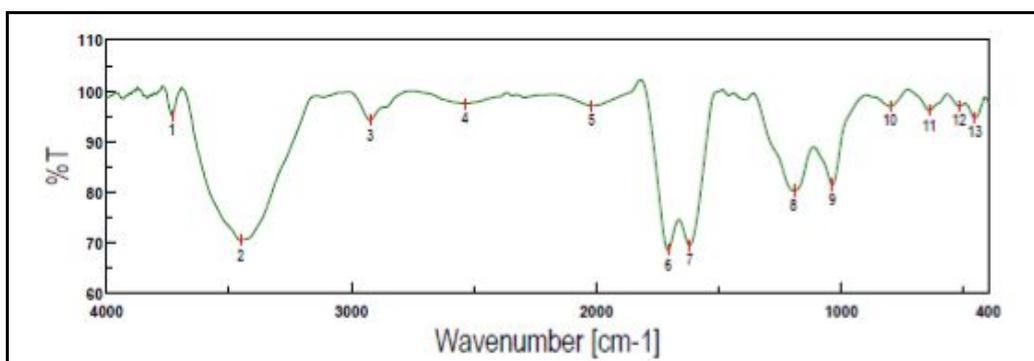


Figure1: FTIR for characterization of TLAC adsorbent

Sorption studies

Adsorption studies were carried out at various concentrations of dyes from 4 mg L^{-1} to 20 mg L^{-1} with 4 mg L^{-1} variation. Increase of initial concentration of RhB increases adsorption capacity, further enhancement of concentration leads to decrease in percentage removal due to non availability of adsorption sites in the adsorbent¹⁸.

Effect of pH The pH is an important parameter which determines and controls the adsorption process. The effect of pH on the percent removal of RhB by TLAC was evaluated with the pH range of 2-8 at initial dye

concentration of 16 mg l⁻¹. Fig. 2 shows the variations of dye at different pH, it is evident from the figure a maximum removal is observed at pH of 6. At low pH, an increase in H⁺ concentration in the solution and acquires positive charge on the surface of TLAC by absorbing H⁺ ions. On the other hand, at higher pH values, a significantly strong electrostatic attraction occurs between the negatively charged surface of the TLAC and cationic dye molecule leading to maximum adsorption of RhB¹⁹. The maximum adsorption occurred at pH 6 and the lowest adsorption at pH 8. Adsorbent surface would be positively charge up to pH 6 and thereafter, becomes negatively charged decreasing the adsorption of RhB.

The dose of adsorbent varied from 0.2 g to 1.0 g L⁻¹. From Fig 3, it can be seen that percentage adsorption of RhB at a dose rate of 0.4 g adsorbent showing higher dye removal when compared with other dosages. The percentage removal of RhB slightly increased with the increase in adsorbent dose is due to the availability of more binding sites for adsorption²⁰. No considerable increment in adsorption with increasing dosage can be attributed to the change in the concentration gradient of dye molecules between the bulk solution and adsorbent²¹.

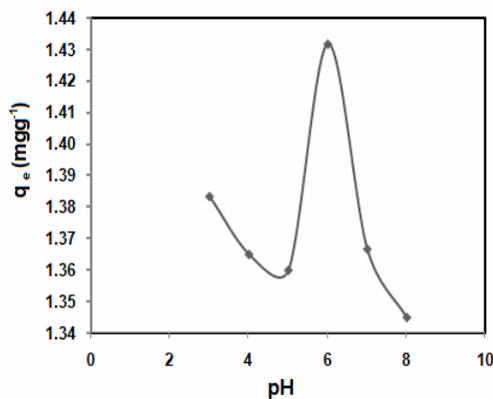


Figure 2 : Effect of pH

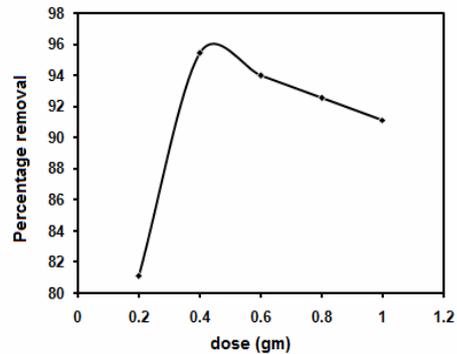


Figure 3 : Effect of adsorbent dose

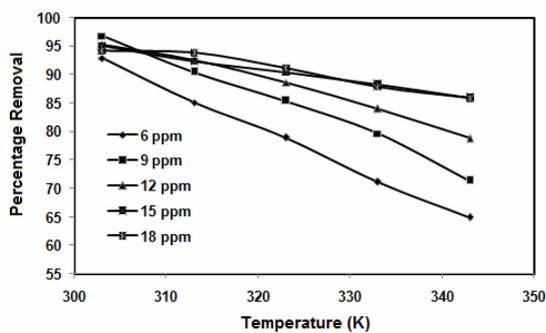


Figure 4 : Effect of Temperature

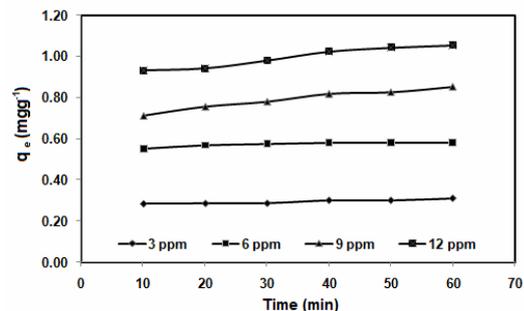


Figure 5 : Effect of contact time

Effect of Temperature

Effect of temperature on adsorption was carried out at temperatures of 303 K, 313 K, 323 K, 333 K and 343 K. These experiments were carried out in the pH 6 with 16 mg L⁻¹ of dye solution on TLAC. The amount of adsorbed RhB dye was decreased with increasing temperature. This can be explained by the fact that the mobility of RhB dye molecules increases with increase in temperature. Fig 4, indicates the decrease in percentage removal could be due to the reduction of the physical forces of attraction between RhB dye and adsorbent. The experimental results showed that the removal of dye is reduced with increase in temperature onto the adsorbent TLAC which is a kinetically controlled exothermic process²². Fig 5, shows the effect of contact time of dye on to TLAC with increase in time the amount of dye adsorbed per unit mass of sorbent slightly increases and attain constant.

Isotherm studies

The adsorption data were analyzed with two adsorption isotherm models, namely Freundlich and Langmuir. Various forms of Langmuir and Freundlich were tested in their linear and non-linear forms^{23, 24}. The Langmuir isotherm is expressed as

$$q_e = q_m K_a C_e / (1 + K_a C_e) \quad \text{-----} [3]$$

The term q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of dye adsorbed per unit mass of sorbent and unadsorbed dye concentration in solution. Where q_m is the maximum amount of dye adsorbed per unit mass of sorbent at complete monolayer on surface bound, and K_a (L mg^{-1}) is a constant related to the affinity of the binding sites.

The Freundlich isotherm equation is expressed as

$$q_e = K C_e^{1/n} \quad \text{-----} [4]$$

Where K (mg g^{-1}) (L g^{-1}) is an indicator of the adsorption capacity, $1/n$ is the adsorption intensity, q_e is the amount adsorbed per unit mass of the adsorbent, C_e the equilibrium concentration.

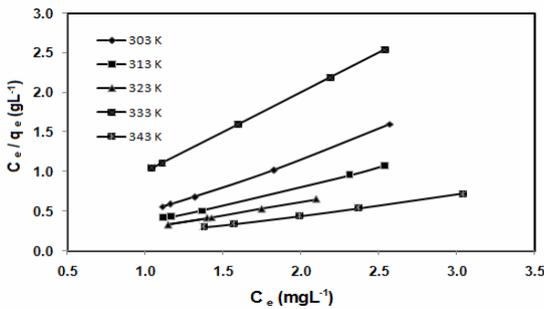


Figure 6 : Langmuir adsorption isotherms

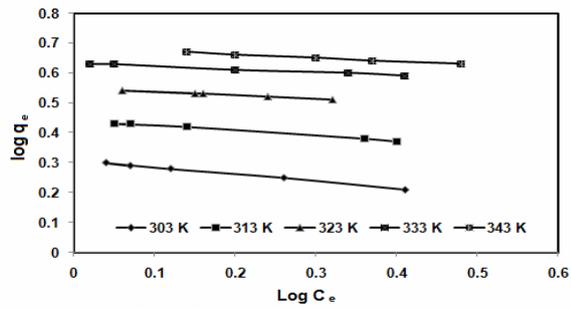


Figure 7 : Freundlich adsorption isotherms

The value of ‘n’ indicates the degree of non-linearity between solution concentration and adsorption. If the value of n is equal to unity, the adsorption is linear; if the value is below unity, this implies that adsorption process is chemical; if the value is above unity, adsorption is a favorable physical process.

Table 1: Isotherm Parameters obtained from Linear Method

Isotherm	Parameters	Temperature (K)			
		303	313	323	343
Freundlich	$1/n$	0.236	0.174	0.115	0.116
	K (mg g^{-1}) (Lg^{-1})	2.032	2.760	3.523	4.830
	r^2	0.997	0.993	0.996	0.991
Langmuir	q_m (mg g^{-1})	1.406	2.155	2.958	3.937
	K_a (L mg^{-1})	2.883	4.000	5.453	4.379
	r^2	0.997	0.999	0.999	0.998

The best suited isotherm model of Freundlich and Langmuir isotherms is used to calculate q_m , K_a and coefficient of determination r^2 that are presented in Table 1. The q_m and K_a values predicted using the parameters of $1/q_e$ vs. $1/C_e$, q_e vs. q_e/C_e and q_e/C_e vs. q_e by plotting graphs. Both Langmuir and Freundlich shows a better correlation coefficient (r^2) value. The higher q_m value of Langmuir confirms that the maximum quantity of adsorption at 303 K.

Using same set of experimental data a plot of $\log(q_e)$ vs. $\log(C_e)$ are used to analyze the linearized form of Freundlich equation. By knowing the r^2 values it was observed that both the Langmuir isotherm and Freundlich isotherm models fitted equilibrium data for all the temperature. Fig. 6, 7 and Table 1 shows experimental data and the predicted equilibrium curves, it clearly indicates that 303 K was found to be more suitable condition. But in the case of other temperatures there was a deviation.

Table 2: Pseudo – first order and second order rate constant for the sorption of RhB

C_0 (ppm)	Pseudo – First order kinetics			Pseudo – second order kinetics			r^2
	K_1	q_e (Cal)	r^2	q_e (Experimental)	K_2	q_e (Calculated)	
15	0.0046	1.355	0.938	0.0311	9.754	0.030	0.994
18	0.0023	1.648	0.830	0.0265	6.642	0.028	0.985

Kinetic studies

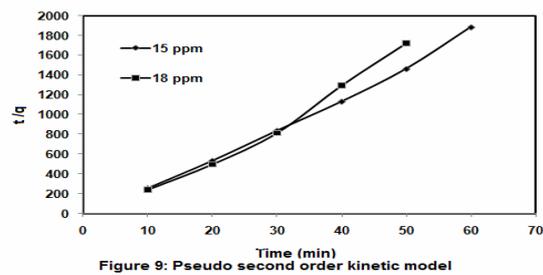
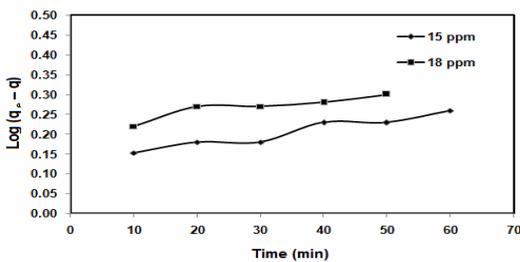
Lagergren’s Pseudo first order (Eq. 5) and Pseudo second order (Eq. 6) kinetic models [25] were applied to study kinetics profiles. The linearized form of the pseudo-first order equation is

$$\text{Log}(q_e - q) = \text{log}(q_e) - K_1 t / 2.303 \quad \text{----- (5)}$$

Where, K_1 is the pseudo first order adsorption rate constant, q_e is the amount of dye adsorbed onto TLAC at equilibrium (mg g^{-1}), q_t amount of dye adsorbed onto TLAC at any time t (mg g^{-1}) The linearized form of the pseudo-second order form is

$$T/q = 1 / K_2 q_e^2 + (1/q_e) t \quad \text{----- (6)}$$

Where, K_2 is the pseudo second order adsorption rate constant, q_e is the amount of dye adsorbed onto TLAC at equilibrium (mg g^{-1}); q_e^2 is the pseudo second order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). Various forms of pseudo-first order and pseudo-second order kinetic equations are presented in the Table 2. From table the coefficient values of pseudo-first order rate constant are very low when compared with pseudo-second order kinetic values. On the other hand the obtained values of pseudo-second order kinetics have shown the correlation coefficient value 0.989 while pseudo-first order shows 0.884. Hence, the results intimate that the sorption process follows second order rate equation throughout the process. Moreover, the rate of the reaction process does not depend on the concentration factor (Pseudo-first order) but depends on both concentration as well as time (Pseudo-second order).



Thermodynamic studies

The effect of heat of adsorption of the adsorbate onto the adsorbent material was determined using the thermodynamic parameters like free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0), were calculated from the Van Hoff’s equation using the following equations^{26, 27}

$$K_d = q_e / C_e \quad \text{---- (7)}$$

$$\Delta G = -RT \ln K_d \quad \text{---- (8)}$$

$$\ln K_d = \Delta S^0 / R - \Delta H^0 / RT \quad \text{--- (9)}$$

Where, K_d is the distribution coefficient, T is the temperature and R is a gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). From Figure 11, the thermodynamic parameters ΔS^0 and ΔH^0 are calculated using the linear regression analysis of Van’t Hoff plot using the parameters $\ln K_d$ vs. $1/T$. The positive value of the enthalpy change of ΔH^0 value shows that the endothermic nature of the reaction involved during the adsorption process. The entropy (ΔS^0) shows positive value, this indicates that there was a increased randomness between the solid-solution interfaces during the adsorption process (Table 3). The Gibbs free energy change (ΔG^0) shows a negative value which reveals that the adsorption process is spontaneous in nature for the adsorption of RhB dye onto TLAC. The kinetic models do not provide enough information of an exact diffusion mechanism that is involved during the process and the rate controlling steps, which affect the nature of the adsorption process²⁸.

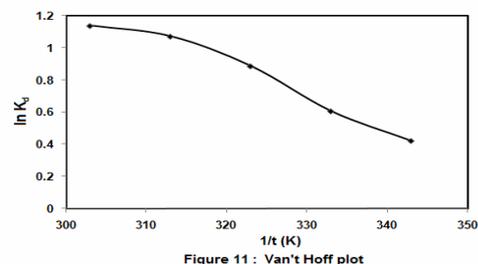
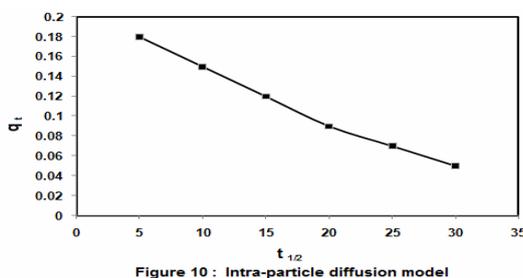


Table 3: Thermodynamic parameters for RhB onto TLAC

T (K)	ΔG° (KJmol ⁻¹)	ΔH° (KJmol ⁻¹)	ΔS° (KJmol ⁻¹ K ⁻¹)
303	-2.87	0.04	57.78
313	-2.79		
323	-2.38		
333	-1.68		
343	-1.20		

The intra particle diffusion equation is given by

$$q_t = K_d t^{1/2} + C$$

Where K_d is intra particle diffusion rate constant and C is intercept. The plot between q_t vs. $t^{1/2}$ shows a straight line and the parameters of K_d and C are calculated from the linear regression analysis of the slope and intercept. The experimental values are depicted in the Figure 10 it shows linearity at different time intervals. The results of r^2 (0.999) and k_d values indicated that the adsorption and intra particle diffusion mechanism are occurring concurrently.

Conclusion

Both Langmuir isotherm and freundlich isotherm was the most favorable method for the adsorption of Rhodamine-B dye. So the adsorption process was favorable for the adsorption of dye onto TLAC. The kinetic result shows that the adsorption process follows pseudo-second order kinetics, which implies that the adsorption process depends on both time and concentration. The thermodynamic parameter change in enthalpy (ΔH°) shows positive value intimating that the adsorption process are endothermic in nature. The Gibbs free energy change (ΔG°) shows a negative value revealing that the adsorption process is spontaneous. The FTIR spectrum shows a well characterized variation with standard peak height and intensity. Experimental studies indicate clearly that TLAC is one of the best cost effective absorbent for the removal of toxic dyes from industrial effluent.

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