

Polymer Composite—A Potential Biomaterial for the Removal of Reactive Dye

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Abstract: Poly Pyrrole saw dust composite was prepared by reinforcement of natural wood saw dust (obtained from *Euphorbia Tirucalli L* wood) and Poly Pyrrole matrix phase. The present study investigates the adsorption behaviour of Poly Pyrrole Saw dust Composite towards reactive dye. The batch adsorption studies were carried out by varying solution pH, initial dye concentration, contact time and temperature. The kinetic study showed that adsorption of Reactive Red by PPC was best represented by pseudo-second order kinetics with ion exchange adsorption. The equilibrium data were analyzed by Freundlich and Langmuir isotherm model. The equilibrium isotherm data were fitted well with Langmuir isotherm model. The maximum monolayer adsorption capacities calculated by Langmuir model were 204.08 mg/g for Reactive Red at 303 K. The thermodynamic parameters suggest the spontaneous, endothermic nature of ion exchange adsorption with weak Vander Waals force of attraction. Activation energy for the adsorption of Reactive by Poly Pyrrole Composite was 11.6387 kJ/mole, Isosteric Heat of adsorption was 48.5454 kJ/mole also supported the ion exchange adsorption process in which forces of attraction between dye molecules and PPC is weak.

Key words: *Euphorbia Tirucalli L* saw dust, polymer composites, Reactive Red, isotherm studies, activation energy, isosteric heat of adsorption.

Introduction

In textile industry, the modern dyeing processes and machinery are designed for the usage of synthetic dyes. Dye containing wastewater discharged from such industries is a serious threat to the receiving water bodies around the industrial areas¹ because these toxic organic dyes can affect plant life and thus destroy the entire ecosystem².

Reactive dyes are extensively used in many textile industries due to their favourable characteristics, and have been identified as problematic compounds in textile wastewater because they are water soluble and found in the waste water at higher concentrations than other dye classes mainly in their spent, hydrolyzed form³⁻⁶. It is estimated that 10-20% of

reactive dyes remain in the waste water during production and nearly 50% of reactive dyes may be lost to the effluents during dyeing process, and their removal from effluent is difficult by conventional physical / chemical as well as biological treatment⁷. Therefore, removal of dyes from effluent becomes environmentally important and many treatment methods have been applied such as physical, chemical and biological methods⁸⁻¹⁰. However these methods have one or more limitations such as low efficiency, high cost, greater energy consumption and generation of sludge. To overcome these problems, there is an urgent requirement for the development of innovative, economic and effective technology, by which dye from the effluent can be removed. A great interest has been recently directed to polymer bio composites for the removal of dyes from waste water. Polymer composites or Green composites are a viable alternative for the exiting waste water treatment technologies. Polymer composites are materials formed by matrix (polymer) and a reinforcement of natural wood fibre derived from renewable resources. These are environmentally friendly, cheap and bio renewable material. Polymer composites would contribute to solve the water pollution problem around the world and could be the efficient and promising adsorbent for the removal of synthetic dyes from aqueous solution. One efficient way of increasing adsorption capacity of saw dust is the polymerization of monomer on the surface of saw dust.

In recent years, conducting electro active polymers such as poly aniline and poly pyrrole have attracted with great attention due to their electrical conductivity and electro activity¹¹⁻¹³. Poly Pyrrole, a conducting polymer doped with releasable or exchangeable counter ions coated on saw dust has been utilized for the removal of anionic dyes from aqueous solutions based on ion exchange properties of these polymers. The dye removal technology utilizing bio composite is a viable option because of its economic, eco-friendly, abundantly available, green way and efficient technique.

In this study, Poly Pyrrole-Saw dust composite prepared by polymerizing pyrrole on saw dust surface via chemical route at room temperature. The main objective of this study is to evaluate the potential of polymer composite (PPC) prepared from Euphorbia Tirucalli wood saw dust. The study includes an evaluation of the effects of various operational parameters such as initial dye concentration, contact time, pH and temperature on the dye removal process. The adsorption kinetic models, equilibrium isotherm models and thermodynamic parameters related to adsorption process were also performed and reported.

Materials and Methods

Adsorbent

Preparation of Poly Pyrrole Composites

Euphorbia Tirucalli L wood saw dust used for the preparation of polymer composite. The saw dust was first washed with distilled water in order to remove impurities and finally dried at 333 K for 2 hours. The poly pyrrole was synthesized on saw dust surface, which was previously soaked in monomer Pyrrole solution (0.2 M) for 12 hour at room temperature followed by slow addition of chemical oxidants 0.5 M FeCl₃ at room temperature for 4 hours¹⁴.

Polymerisation was carried out on the surface of saw dust immediately after the addition of oxidant solution. The polymer coated saw dust designated as PAC were filtered, washed with distilled water and dried.

Character Studies

Physico-chemical characteristics of Poly Pyrrole composite were studied as per the standard testing methods^{15, 16}. In order to characterize the surface structure and morphology of Poly

Pyrrole saw dust composite, SEM analysis was carried out using Scanning Electron Microscope as shown in Figure 1.

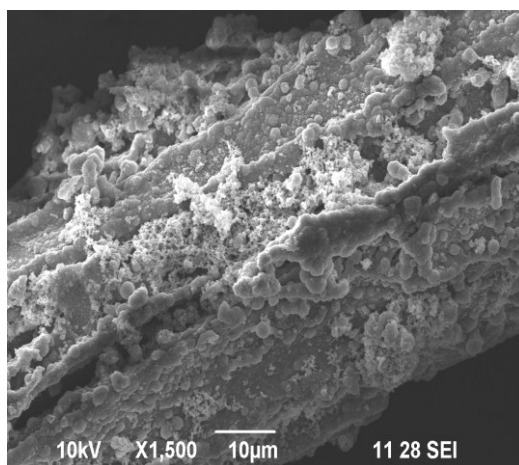


Figure 1. SEM image of PPC.

Adsorbate

Reactive Red195 (M.Wt:1136.31, Mol. Formula: $C_{31}H_{19}ClN_7O_{19}S_6Na_5$, λ_{max} : 543 nm) used in this study were of commercial quality and used without further purification. The structure of Reactive Red 195 is shown in Figure.2.

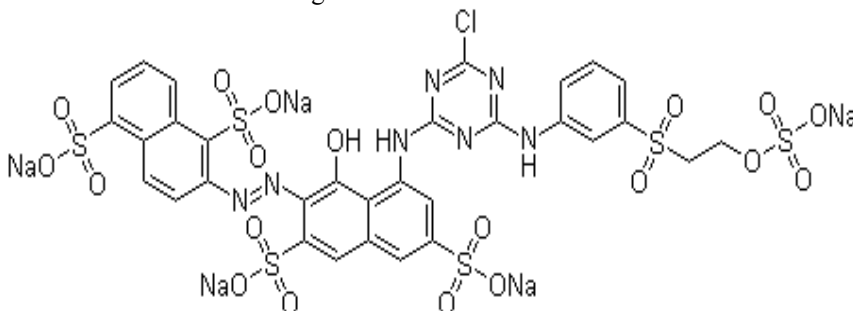


Figure 2. Structure of Reactive Red.

A stock solution of Reactive Red 195 was prepared by dissolving appropriate amount of dye (based on the percentage purity) and suitably diluted as and when required. The concentration of the dye was determined using Elico make UV-Vis spectrophotometer at wavelength 543 nm. All chemicals used were analytical reagent grades and used without further purification.

Experimental Procedure

Batch Adsorption Experiments

Adsorption experiments were conducted at room temperature by agitating 0.10 gm of adsorbent with 100 ml of dye solution of desired concentration in 250 ml stoppered flask

using a shaker at a speed of 120 rpm for equilibrium time except for contact time experiments. The effect of solution pH on the equilibrium adsorption of dyes (50 mg/L) was investigated under similar experimental conditions between pH 2 to 12. The effect of temperature on the equilibrium adsorption was studied under similar conditions between temperatures of 303 to 318 K.

Equilibrium Isotherm Studies

Equilibrium studies were conducted by agitating 100 ml of dye solution with 0.1 gm of adsorbent at different initial dye concentration (10-170 mg/lit) upto equilibrium time. After equilibrium, the solution was analysed for remaining dye concentration using Elico make UV-Vis spectrophotometer at appropriate wavelengths. The equilibrium experiments were conducted at different temperatures.

Result and Discussion

Analysis of Adsorbent Characteristics

The Physico-chemical characteristics of PPC prepared from *Euphorbia Tirucalli L* wood was summarised in Table 1.

Table 1 - Physico-chemical characteristics of Poly Pyrrole Composite.

S.No	Properties	PPC
1	pH	7.81
2	Moisture content, %	9.85
3	Conductivity, $\mu\text{S/cm}$	5.86
4	Volatile matter, %	54.8
5	Methylene Blue value, mg/g	41
6	Iodine Number, mg/g	98

Analysis of Adsorption Parameters

Effect of initial dye concentration and contact time

The rate of adsorption is a function of the initial dye concentration and contact time which is an important factor for the effective adsorption. The Figure.3 depicts the adsorptions of RR195 by PPC at various initial dye concentrations with contact time. When the initial dye concentration increased from 25 to 100 mg/L, the adsorption capacity of PPC increases from 46.88 to 157.33 mg/g, but the percentage of dye adsorption decreases from 93.75 to 78.67%. The percentage removal of dyes decreases when the initial concentration increases from 25 to 100 mg/L for PPC because the adsorbent has a limited number of active sites which becomes saturated at a certain concentration. Similar results have been observed for the removal of Eosin Y using conducting electro polymers ¹⁴, adsorption of Reactive Orange on loofa activated carbon ¹⁷. The equilibrium adsorption increased with rise in contact time and equilibrium reached at 60 minutes for RR195. Initially the rate of adsorption was rapid, slow and reaches equilibrium, further increase in contact time did not enhance the adsorption. The initial rapid adsorption may be attributed to the presence of large number of available binding sites for adsorption and slower adsorption is due to saturation of binding sites and equilibrium attained.

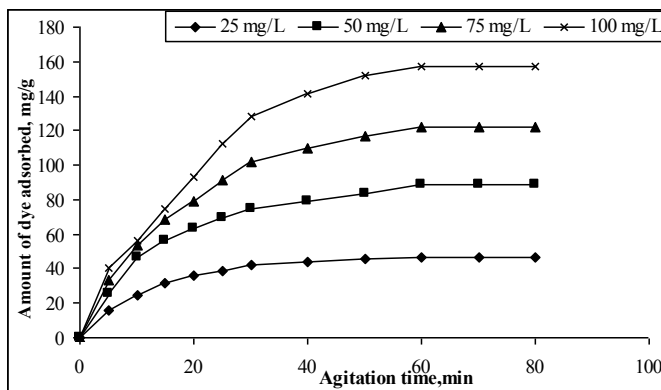


Figure 3. Effect of Initial Dye concentration and contact time for the adsorption of RR onto PPC.

Effect of pH

The pH of the dye solution has been recognized as one of the most important factors influencing the adsorption process. The effect of initial pH on the dye removal efficiency of PPC was studied at different pH ranging from 2-12 and shown in Fig.4. The adsorption of RR195 was pH dependent. The maximum percentage removal of RR195 occurs at acidic pH 3-4 and adsorption decreases with increase in pH. In acidic medium, the surface of the adsorbent is positively charged due to higher concentration of H^+ ions, so the electrostatic attraction between PPC and RR195, is enhanced. But in alkaline conditions, electrostatic repulsion occurs resulting in decreased adsorption. Similar results have been reported for the adsorption of Eosin Y using conducting electro polymers¹⁴.

Effect of Temperature

The effect of temperature on dye adsorption was studied at 30, 35, 40 and 45° C. The results indicated that the amount of dye adsorbed at equilibrium increases with increasing temperature. This may be a result of increase in the mobility of the dye molecules with increase in temperature¹⁸. The equilibrium adsorption increased from 88.37% to 95.35% for RR195, indicates that the adsorption is endothermic process.

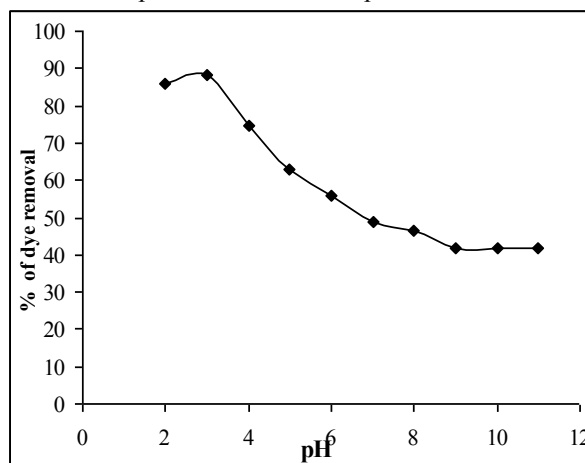


Figure 4. Effect of pH for Adsorption of Reactive Red onto PPC.

Adsorption Kinetics

In order to investigate the mechanism of adsorption, characteristic constants of adsorption were determined using Pseudo-first order equation¹⁹ of Lagergren based on solid capacity and Pseudo- second order equation²⁰ based on solid phase adsorption.

Pseudo-first order Lagergren kinetic equation can be expressed as follows

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

The integrated form of equation

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

The dye adsorption described by a modified second order equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

The values of second order rate constant k_2 and q_e were calculated from the intercepts and slopes of the plot of t/q_t vs t as shown in Figure.5 and the results are summarized in table 2.

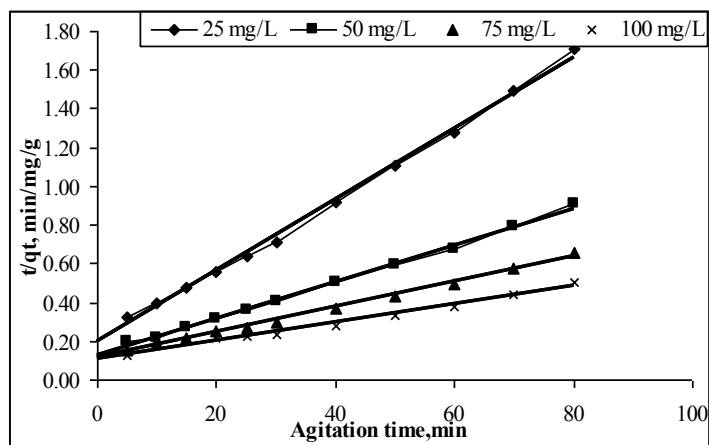


Figure 5. Pseudo-Second Order plot for Adsorption of RR onto PPC.

The value of k_2 decreases with increase in dye concentration due to decrease in available vacant sites for adsorption. The values of r^2 suggested that pseudo first order equation does not fit well with whole range of adsorption process, as it is applicable for the initial stages of adsorption processes²¹. Based on the values of correlation co-efficient which is above 0.98, the second order kinetic model was more suitable to describe the adsorption process for reactive dye adsorption than pseudo-first order model. But to identify the mechanism of adsorption, the kinetic results were further analysed by ion exchange process.

Table 2. Kinetic Model values for adsorption of Reactive Red.

Concn mg/L	First Order Kinetics			Second Order Kinetics		
	k_1 (min ⁻¹)	$q_e(\text{cal})$ (mg/g)	r^2	$\frac{k_2 \times 10^{-4}}{10^{-4}}$ (g/mg min)	$q_e(\text{cal})$ (mg/g)	r^2
25	0.0677	43.33	0.9945	17.3606	54.35	0.9974
50	0.0568	80.43	0.9946	7.1236	105.26	0.9978
75	0.0612	130.23	0.9901	3.6995	153.85	0.9953
100	0.0652	193.02	0.9694	1.9813	212.76	0.9826

Ion Exchange Process

In case of polymer saw dust composite the increase in adsorption capacity is due to its ion exchangeable active sites. Poly Pyrrole has positively fixed charged sites which are balanced with the anion. The small size dopant anions can be exchanged with other anionic species in the dye solutions which have stronger interactions with the polymer¹⁴. Therefore, higher percentage removal of anionic dyes by the polymer saw dust composite is supposed to occur by ion-exchange mechanism due to exchangeable active sites and explained by pseudo-second order kinetics. However, the importance of other processes such as electrostatic interactions between highly polar and positively charged polymer and negatively charged anionic dye molecules cannot be ignored.

Adsorption Isotherm

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between adsorbate and adsorbent. It is important for predicting the adsorption capacity of adsorbent, which is the main parameters required for design of an adsorption system.

The Langmuir²² and Freundlich²³ models were used to describe the adsorption of RR onto PPC.

The Langmuir equation can be written as

$$\frac{c_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{c_e}{Q_0} \quad (4)$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and b_L (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. This equation has been successfully applied to many adsorption processes. The Langmuir isotherm is based on assumption of structurally homogeneous adsorbent and monolayer coverage with no interaction between the sorbate molecules. Once a dye molecule occupies a site, no further adsorption can take place at that site²⁴. The values of Q_0 and b_L calculated from the slopes and intercepts of the linear plots of C_e/q_e vs C_e as shown in Figure 6 and the results are summarized in table 3.

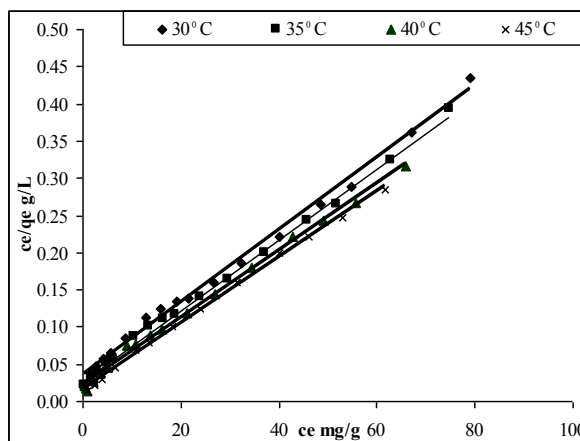


Figure 6. Langmuir Isotherm for Adsorption of RR onto PPC.

The values of adsorption efficiency Q_0 and adsorption energy b_L increases with increasing the temperature suggested that the maximum adsorption corresponds to a saturated monolayer of dye molecules on all the adsorbents. Further it confirms the endothermic nature of processes involved in the system²⁵. The maximum adsorption capacity Q_0 varies from 204.08 to 222.22 mg/g for RR while increasing the temperature from 30°C to 45°C.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L ²⁶ that is defined by the following equation

$$R_L = \frac{1}{(1 + bC_0)} \quad (5)$$

Where, C_0 is the highest initial solute concentration. R_L value indicated the type of adsorption isotherm to be either unfavourable ($R_L > 1$), favourable ($R_L < 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). Langmuir model is more appropriate to explain the nature of adsorption of RR with correlation coefficient of 0.994 to 0.9979.

Table 3. Comparison of the coefficients of Isotherm parameters of Reactive Red.

Temp °C	Isotherm Models					
	Langmuir				Freundlich	
	Q_0 (mg/g)	b_L (L/mg)	r^2	n	k_f ($\text{mg}^{1-1/n}$ $\text{L}^{1/n} \text{g}^{-1}$)	r^2
30	204.08	0.1400	0.9940	2.5012	39.9484	0.9467
35	208.33	0.1846	0.9966	2.8050	50.1674	0.9613
40	222.22	0.2036	0.9967	2.9334	57.6702	0.9547
45	222.22	0.2960	0.9979	3.2030	69.1035	0.8841

The Freundlich model is employed to describe the heterogeneous system, which is characterized by heterogeneity factor $1/n$. It considers multilayer adsorption with heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules. The Freundlich isotherm is expressed as

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \quad (6)$$

Where, K_f and $1/n$ are Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent respectively. Q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g); c_e is the equilibrium concentration of adsorbate (mg/L). The values of K_f and $1/n$ are calculated from intercept and slopes of linear plot of $\log q_e$ versus $\log c_e$ (figure not shown). The value of $1/n$ is below one for RR studied indicating that the adsorption of dyes is favourable. The results of isotherms are summarized in Table.3.

An analysis of the correlation coefficients obtained for these isotherms showed that both isotherm equations describe the adsorption, but Langmuir model was found to be more appropriate to explain the adsorption of RR onto PPC.

Thermodynamic Parameters

Activation Energy

The second order rate constant of the dye adsorption is expressed as a function of temperature by Arrhenius relationship.

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (7)$$

where E_a and A refers to Arrhenius activation energy and Arrhenius factor obtained from the slope and intercepts of a graph by plotting $\ln k_2$ vs $1/T$ as shown in Fig 7. The activation energy was found to be 11.6387 kJ/mole for adsorption of RR onto PPC. The physisorption usually have energies in the range of 5-40 kJ/mole, while higher activation energies 40-800 kJ/mole suggests chemisorption²⁷. The activation energy < 40 KJ/mole for RR dye indicates the physisorption.

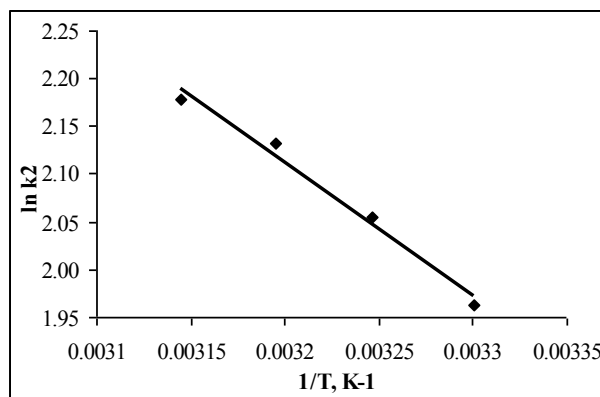


Figure 7. Arrhenius plot for Adsorption of AO10 onto PAC.

In adsorption process, energy consideration must be taken into account in order to determine what process will occur spontaneously. Thermodynamic parameters values are the actual indicators for practical application of a process²⁸.

The thermodynamic parameters such as change in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) can be determined by using VanthHoff equation

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \dots (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \dots (9)$$

Where, T is the absolute temperature and K_L (L/g) is the standard thermodynamic equilibrium constant. By plotting a graph of $\ln K_L$ vs $1/T$, the values of ΔS^0 and ΔH^0 can be estimated from the slopes and intercepts (figure not shown). The results are summarized in Table 4. The Gibbs free energy change (ΔG^0) is an indication of spontaneity of a chemical reaction therefore it is an important criterion for spontaneity. The change in free energy for physisorption is between -20 and 0 kJ/mole, but chemisorption is in a range of -80 to -400 kJ/mole²⁹⁻³⁰. The values of ΔG^0 for all the three dyes were within the range of -20 and 0 kJ/mole, indicating that the physisorption is the dominating mechanism. The positive values of ΔS^0 confirming physical adsorption nature and increased randomness at the solid-solution interface during adsorption and indicate affinity of the dye onto adsorbents³¹. Physisorption and chemisorptions can be classified to a certain extent by the magnitude of enthalpy change. Bonding strengths of <84 kJ/mole are typically considered as those of physisorption bonds. Chemisorption bond strengths can be 84-420 kJ/mole³².

Isosteric Heat of Adsorption

Isosteric Heat of Adsorption ΔH_X is defined as the heat of adsorption determined at constant amount of adsorbate adsorbed. It is the basic requirements for the characterization and optimization of an adsorption process and also very important for equipment and process design.

The isosteric heat of adsorption at constant coverage is calculated using Clausius – Clapeyron equation³³

$$\ln Ce = \frac{\Delta H_X}{RT} + K \quad \dots (10)$$

Where, Ce is the equilibrium dye concentration in solution (mg/L), ΔH_X is the isosteric heat of adsorption (kJ/mole). The isosteric heat of adsorption is calculated from the slope of the plot $\ln Ce$ versus $1/T$ (figure not shown) is given in table 4. The magnitude ΔH_X provides an information about the nature and mechanism of the process. For physical adsorption ΔH_X should be below 80 kJ/mole and for chemical adsorption it ranges between 80-400 kJ/mole³⁴.

Table 4. Thermodynamic Parameters at different Temperatures.

Temp°C	ΔG^0	ΔH^0	ΔS^0	Ea	ΔH_X
	kJ/mol	kJ/mol	kJ/K/mol	kJ/mole	kJ/mole
30	-8.4306				
35	-9.2735				
40	-10.1164	42.6474	0.1685	11.6387	48.5454
45	-10.9592				

The value of ΔH_X for the adsorption of RR onto PPC is 48.5454 kJ/mole which is within the range of physisorption and suggested that the adsorption process is physisorption. Therefore, the values of ΔG^0 , ΔH^0 , ΔH_X and Ea all suggest that adsorption of RR onto polymer coated

saw dust was driven by ion exchange adsorption process involving weak Vander Walls force of attraction (as the adsorption energy is very less).

Conclusion

The present investigation showed that Poly Pyrrole – saw dust composites can be effectively and efficiently used for the removal of Reactive dyes from aqueous solution. The adsorption process was dependent on pH, maximum adsorption occurs at pH 3-4 for RR. The pseudo-second order kinetic model fitted well with the dynamical adsorption behavior of anionic dyes suggested ion exchange adsorption. The maximum monolayer adsorption capacities calculated by Langmuir model were 204.08 mg/g for Reactive Red at 303 K. The adsorption capacity of PPC increased with rise in temperature indicating endothermic nature of adsorption. The thermodynamic parameters such as enthalpy change, free energy change indicated the physisorption nature of adsorption process. Arrhenius activation energy calculated was 11.6387 kJ/mole on PPC and lower values of isosteric heat of adsorption also supported the forces of attraction between dye and Poly Pyrrole Composite was weak. Lower bonding energy suggested that only weak bond is formed between dye and polymer composite. Based on the results obtained in this study, it can be concluded that Poly Pyrrole composite is an effective, economic and alternative biomaterial for the removal of Reactive dyes.

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