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Kinetics and Equilibrium Studies on The Removal of Anionic Dyes using Polyaniline Coated Sawdust Composite

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Abstract: The feasibility of polyaniline coated sawdust composite (PAn/SD) prepared from the fruit of the gardening plant material *Cordia sebestena* for the adsorption of anionic dyes namely Direct Green 6 (direct dye) and Reactive Orange 16 (Reactive dye) was investigated. Batch mode kinetic and isotherm studies were analysed to evaluate the effects of contact time, initial dye concentration, pH and temperature. The maximum percentage removal of Direct Green 6 was 76.83% and Reactive Orange 16 was 79.50%. at an initial dye concentration of 50 mg/L at 30^0C. Adsorption kinetic data was studied using Pseudo first order and second order models. The equilibrium isotherm data were analyzed by Freundlich and Langmuir isotherm models. The maximum adsorption capacity Q_0 varies from 217.39 mg/g to 135.13 mg/g for DG6 and 100 mg/g to 123.45 mg/g for RO16 while increasing the temperature from 30°C to 50°C. Thermodynamic parameters were also evaluated and it was found to be spontaneous, endothermic and physical adsorption in nature. The results showed that the polyaniline coated sawdust (PAn/SD) synthesised from the fruit of the plant material Cordia Sebestena was suitable for the removal of the anionic dyes from the aqueous solutions.
Keywords: Cordia Sebestena, polyaniline coated sawdust composite, anionic dyes, adsorption, kinetics and isotherm studies.

Introduction

The effluents from the dyestuff manufacturing and textile industries are highly colored with a large amount of suspended organic solids and considered as important sources of water pollution[1]. The removal of dyes from colored effluents, particularly from textile industries is one of the major environmental concern these days [2,3]. Several methods have been employed to remove dyes from the wastewater such as physical and chemical processes. Amongst the various commercial processes, color removal using activated carbon has great potential[4,5,6,7]. Due to high cost of activated carbon, now research is turn into the use of low cost cheaper materials as adsorbents. Though several studies using cheaper material as adsorbents have successfully applied for removing different kinds of dyes from aqueous solution, only few of them could be employed effectively. A great interest has been recently directed to polymer bio composites for the removal of dyes from wastewater. One efficient way of increasing adsorption capacity of saw dust is the polymerization of monomers on the surface of sawdust[8]. In recent years, conducting electro active polymers such as polyaniline and polypyrrole have attracted with great attention due to their electrical conductivity and electro activity[9,10,11].

Hence in the present study, the fruit of the gardening plant material Cordia Sebestena considered to be a waste has been used effectively as an adsorbent. Its fruit is the source for making sawdust and then the polyaniline which is an conducting polymer is coated onto the sawdust. Thus the prepared polyaniline coated sawdust composite was used as an adsorbent for the removal of two different types of dyes namely Direct Green 6 and Reactive Orange 16 from aqueous solutions. The study includes an evaluation of the effects of various parameters like initial dye concentration, contact time, pH and temperature. The adsorption kinetic

models, equilibrium isotherm models and thermodynamic parameters related to adsorption process were also performed and reported.

Experimental

Adsorbent

Polyaniline coated sawdust composite (PAn/SD) was prepared on sawdust surface of the fruit of Cordia Sebestena. In order to prepare PAn/SD, 5.0g of sawdust immersed in 50 mL of 0.20 M freshly distilled aniline in 1 M HCl solution for 6 hours before polymerization. The excess of the monomer solution was removed by simple decantation. 50 mL of oxidant solution 0.20 M $(NH_4)_2S_2O_8$ was added into the mixture gradually and the reaction was allowed to continue for 4 hours at room temperature. Polyaniline coated sawdust composite (PAn/SD) was filtered, washed with sufficient distilled water and then was dried in an oven at temperature about 60 °C and sieved before use.[12]

Adsorbate

The dyes used were Direct Green 6 (DG6) and Reactive Orange 16 (RO16) which are anionic in nature. The stock solution was prepared by dissolving 1g of dye in water and upto 1000ml using double distilled water. The concentration of the dye solution was determined by using UV-Vis spectrophotometer (Elico make BL 198) at its wavelength.

Direct Green 6 (DG6)
Chemical formula: $C_{34}H_{22}N_8Na_2O_{10}S_2$, C.I.No: 30295, M.W: 812.69, λ_{max}:623nm
Reactive Orange 16 (RO16)
Chemical formula : $C_{20}H_{17}N_3\ Na_2O_{11}S_3$, C.I No: 17757, M.W: 617.54, λ_{max}: 494nm

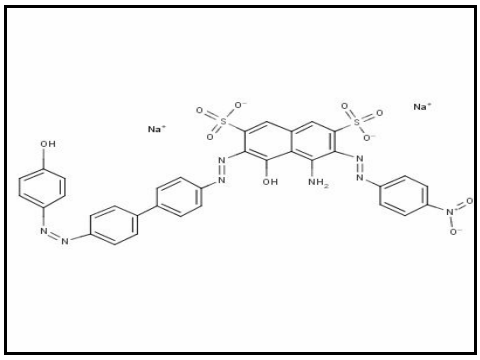


Fig.1a Structure of Direct Green 6

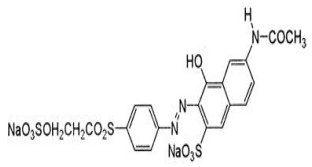


Fig.1b Structure of Reactive Orange 16

Characterization study

FT IR:

Infrared spectra of polyaniline coated sawdust (PAn/SD) and sawdust of the fruit material (SD) measured with a Fourier transform infrared spectrophotometer (Fig.2a& 2b) to elucidate the functional group presenting in PAn/SD and SD and the results were given in Table 1.

Table 1: Peak assignments of functional groups of SD & PAn/SD

Peak positions/Samples		Possible assignments	References
SD	**PAn/SD**		
3344.93	-	O-H stretching	14
2923.56	2922.59	C-H stretching	15,18
1726.94 1625.7	1592.91 1496.49	C=O str of carbonyl group	16,17
1419.35 1319.07 1265.07 1033.66	- 1307.5 1149.37 1029.8	C-O str and OH bending of alcohol and carboxylic acids	13,17
-	815.74	-CH def	20
619.038	-	C-C stretching	19
-	597.82 511.04	C-X group	21

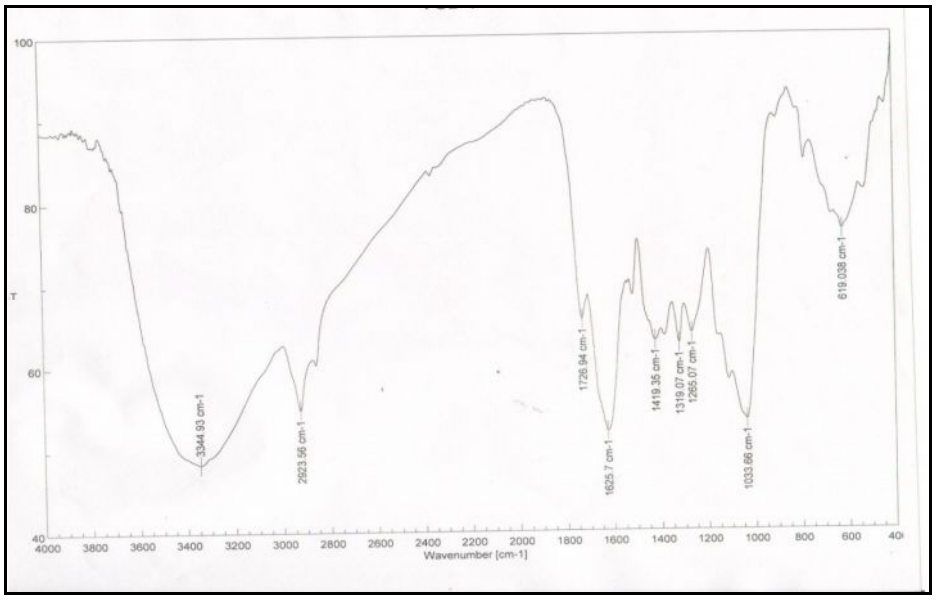


Fig.2a FTIR spectra of SD

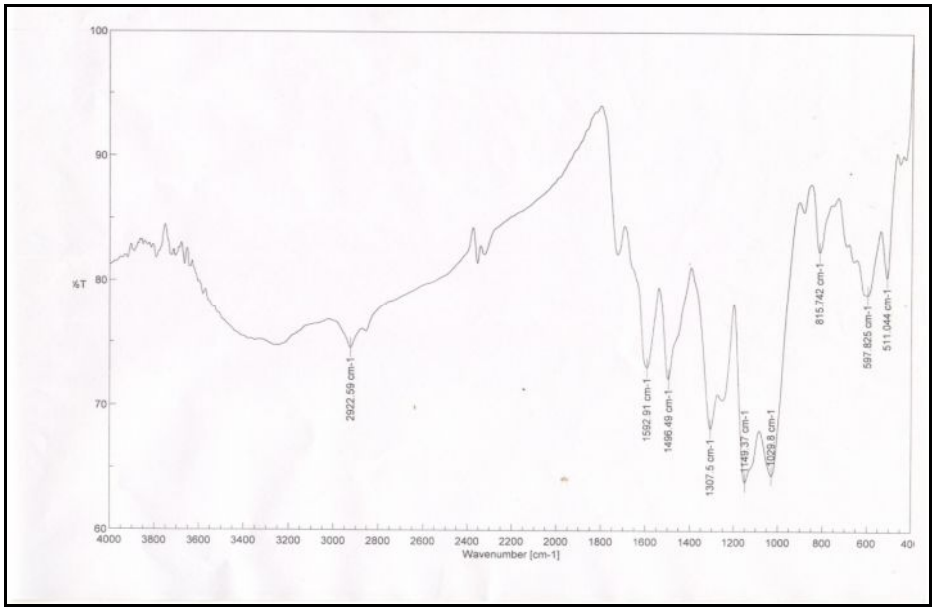


Fig.2b FTIR spectra of PAn/SD

From the FTIR spectra (Fig.2a & 2b) of SD and PAn/SD, we inferred that some of the peaks in SD has been disappeared when it is coated with the polymer polyaniline. This proves the formation of PAn/SD over SD. The peak at 3344.3 cm^{-1} in SD which corresponds to O-H stretching is not found in PAn/SD. It confirms that polymer could be coated over the sawdust. The peak at 815.4cm^{-1} corresponds to –CH def founds only in the FTIR of PAn/SD. The peak at 619.038 cm^{-1} corresponds to out of plane C-H bending mode was not found in PAn/SD. It indicates that the polymer polyaniline has been coated over the saw dust of fruit of *Cordia Sebestena*. The presence of the above said functional groups may be attributed for the effective dye removal in PAn/SD.

Batch Experiments

Batch adsorption experiments were conducted by agitating 100 mg of adsorbent with 100 mL aqueous solution of dyes (DG 6 & RO16) at different concentrations (25 to 100 mg/L), temperatures (30°C, 40°C, 50°C) and pH values. The pH values ranged from 2.0 to 11.0 using HCl and NaOH for its adjustment. The adsorbent was removed by centrifugation and the concentration of dye in the supernatant liquid was determined spectrophotometrically (Elico make: model BL 198).

Results and Discussion

Effect of initial dye concentration

The results from the study indicate that the percentage removal of DG6 decreases from 78.82% to 72.96% and for RO16, it decreases from 82.33% to 75.48% when the initial concentration increases from 25 to 100 mg/L with PAn/SD. Thus on increasing the initial concentration of dye, the percentage removal of dye gets decreased. The decrease in percentage is due to less number of available active sites for adsorption. The results were shown in fig.3a & 3b. But the amount of dye adsorbed per unit mass of adsorbent increased.

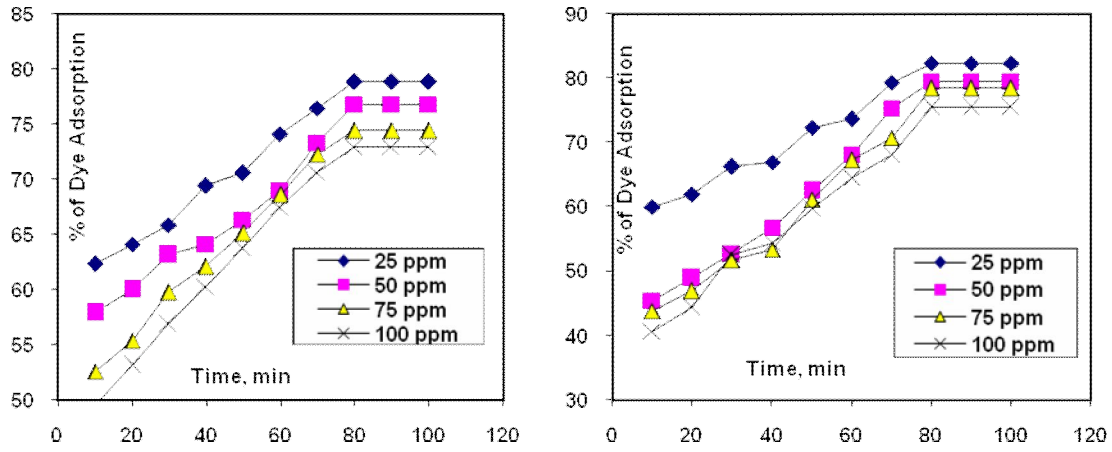


Fig.3a Effect of agitation time on the percentage removal of DG6 dye at 30°C

Fig.3b Effect of agitation time on the percentage removal of RO16 dye at 30°C

Effect of contact time

The results from the study showed that when time increases, the percentage removal goes on increases and attain equilibrium at a particular time period. The maximum percentage of dye removal at equilibrium time for DG6 was 76.83% and RO16 was 79.50% for 50ppm of dye concentration. Thus 100 minutes is fixed as the optimum contact time for both the dyes. The results were shown in fig.3a & 3b.

Effect of pH

The maximum percentage removal of DG6 was 81.33% and RO16 was 81.82%. The results were shown in fig 4. From the above results, it is clear that the removal of dyes is more at lower pH. In the low pH (acidic condition), the positive surface charge of absorbent (PAn/SD) increases and this could attract the negatively charged functional groups on the direct and reactive dyes. The number of negatively charged sites

increases when the pH is increased. Thus there will be a competition between the negatively charged hydroxyl ions and anionic dyes for the sorption sites and the adsorption rate gets decreased [22].

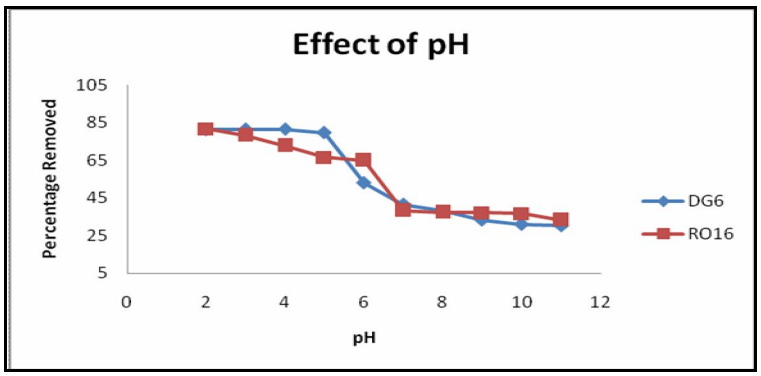
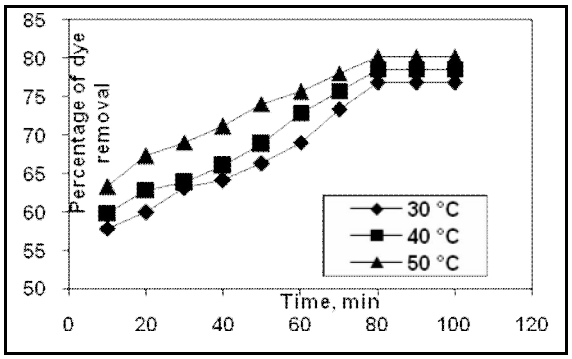


Fig.4 Effect of pH of DG6 & RO16

Effect of temperature

The results from the study indicated that the percentage removal of DG6 and RO16 by PAn/SD increases from 76.83% to 80.24% and 79.50% to 86.83% while increasing the temperature from 30°C to 50°C and the results are shown in fig 5a& 5b. This indicates that the sorption of DG6 and RO16 onto PAn/SD is endothermic in nature.



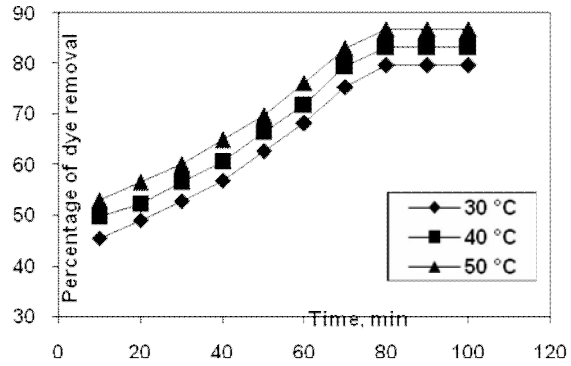


Fig.5a Effect of temperature on the adsorption of DG6 dye at initial concentration of 50mg/L

Fig.5b Effect of temperature on the adsorption of RO16 dye at initial concentration of50mg/L

Adsorption kinetics

For evaluating the adsorption kinetics of DG6 and RO16, Lagergren first order and Pseudo second order models were used to fit the experimental data. The Lagergren first order equation is expressed as [23]

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) t$$

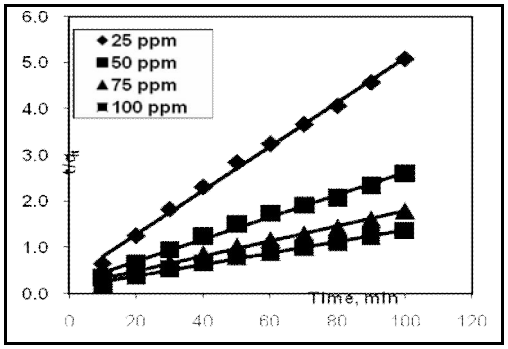
where, q_e = is the amount of adsorbate adsorbed at equilibrium (mg/g), q_t= is the amount of adsorbate at time t (mg/g), K_1 = is the first order rate constant (mm^{-1}) and t is time (min). From the slopes and intercepts of plot of log (q_e -q_t) vs t obtained for the sorption of DG6 and RO16, the first order rate constant K_1 and the calculated q_e (q_e cal) values were determined. The results are given in Table 2a & 2b. The correlation coefficients for the first-order kinetic model obtained were low for both the dyes. Therefore, the systems were not fit to first order model.

The pseudo second order equation is expressed as [24]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

where, K_2 = rate constant of the pseudo second order adsorption (g/mg.min), q_e = equilibrium adsorption capacity (mg/g). From the slopes and intercepts of the plots t/q vs t obtained for the sorption of DG6 and RO16,

the second order rate constant K_2 and the q_e cal were determined. The results are shown in Table 2a & 2b and in fig 6a & 6b and 7a & 7b. The second order model shows satisfactory fit with the experimental data for the sorption of DG6 and RO16 onto PAn/SD with high correlation coefficients. In addition to that, the calculated q_e value shown in Table 2a & 2b were quite similar to the experimental values.



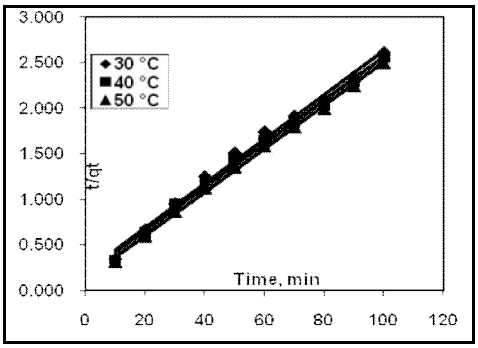
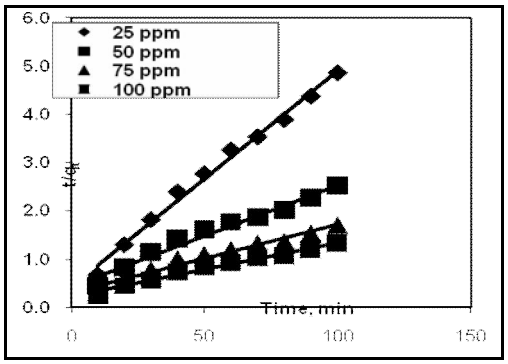


Fig.6a Pseudo second order plots for the adsorption of DG6 dye at different initial dye concentrations

Fig.6b Pseudo second order plots for the adsorption of DG6 dye at different temperatures



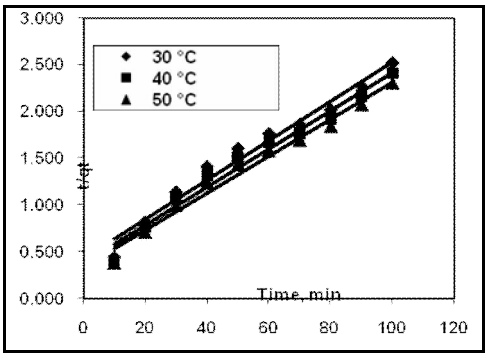


Fig.7a Pseudo second order plots for the adsorption of RO16 dye at different initial dye concentrations

Fig.7b Pseudo second order plots for the adsorption of RO16 dye at different temperatures

Table 2a: Kinetic Model values for adsorption of DG6 and RO16 onto PAn/SD at various initial concentrations

Dyes	Conc mg/L	First order Kinetics			Second order kinetics		
		k_1 (min^{-1})	q_e cal(mg/g)	r^2	$k_2 \times 10^{-4}$ (g/mgmin)	q_e cal(mg/g)	r^2
DG6	25	0.03063	7.0485	0.8977	71.8	20.92	0.9966
	50	0.02441	14.1807	0.8573	28.1	41.32	0.9923
	75	0.03478	29.7029	0.8812	17.1	60.98	0.9947
	100	0.03593	42.7464	0.9097	11.7	80.65	0.9945
RO16	25	0.02925	9.3864	0.8389	46.4	22.42	0.9921
	50	0.03109	30.4508	0.8389	10.4	47.62	0.9734
	75	0.02533	40.0036	0.9209	6.5	70.92	0.9678
	100	0.02556	50.5358	0.9636	5.4	90.09	0.9791

Table 2b: Kinetic Model values for adsorption of DG6 and RO16 onto PAn/SD at various temperatures

Dyes	Conc mg/L	First order Kinetics			Second order kinetics		
		k_1 (min^{-1})	q_e cal(mg/g)	r^2	$k_2 \times 10^{-4}$ (g/mgmin)	q_e cal(mg/g)	r^2
DG6	30	0.02441	14.1807	0.8573	28.1	41.32	0.9923
	40	0.02902	15.5847	0.8659	29.3	42.19	0.9941
	50	0.03132	13.2525	0.9356	40.7	42.37	0.9979

RO16	30	0.03109	30.4508	0.8389	10.4	47.62	0.9734
	40	0.03201	31.0313	0.8272	11.0	49.02	0.9769
	50	0.03201	30.7822	0.8435	11.7	50.51	0.9806

Adsorption isotherm

For evaluating the adsorption isotherms of DG6 and RO16, Langmuir and Freundlich equations were used. The linearized form of the Langmuir isotherm equation is represented as [25]

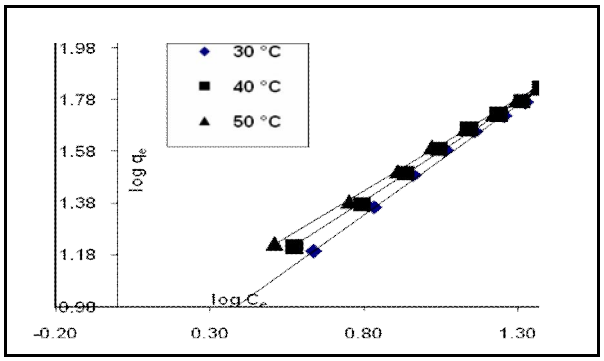
$$\frac{C_e}{q_e} = \frac{1}{b_L Q_0} + \left(\frac{1}{Q_0}\right) C_e$$

Where q_e is equilibrium amount of solute adsorbed per unit weight of adsorbent (mg/g); C_e is equilibrium concentration (mg/l); Q_0 is the maximum amount adsorbed per unit mass of adsorbent (mg/g); b_L is a constant related to the affinity of the binding sites and energy of adsorption in (L/mg). A plot of C_e/q_e vs C_e would give the value of Q_0 and b_L from the slope and intercept respectively.

The linearized form of the Freundlich isotherm equation is represented as [26]

$$\log q_t = \log k + \frac{1}{n} \log c_e$$

where C_e, the equilibrium dye concentration in solution (mg/L); k, the Freundlich constant (mg/g (L/mg), 1/n which represents the adsorption capacity and 'n' is the heterogeneity factor. A plot of log q_e versus log C_e would give the value of 1/n and k from the slope and intercept respectively. The results of both Langmuir and Freundlich adsorption isotherm models were given in Table 3 and the Freundlich adsorption isotherm plots were represented in fig.8a & 8b.



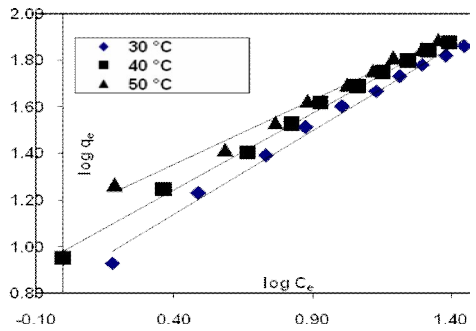


Fig.8a Freundlich plot for the adsorption of DG6 dye

Fig.8b Freundlich plot for the adsorption of RO16 dye

Table 3: Comparison of the coefficients of isotherm parameters of DG6 & RO16

Dyes	Temp ^{0}C	Isotherm models					
		Langmuir			Freundlich		
		Q_0 (mg/g)	b_L (L/mg)	r^2	n	k ($mg^{1-1/n}L^{1/n}\ g^{-1}$)	r^2
DG6	30	217.3913	0.018053	0.9821	1.17	4.4709	0.9973
	40	166.6667	0.027933	0.9670	1.30	5.902	0.9985
	50	135.1351	0.041364	0.9411	1.40	7.1795	0.9992
RO16	30	100	0.059207	0.9905	1.40	7.1466	0.9915
	40	114.94253	0.069157	0.9629	1.52	9.5609	0.9961
	50	123.45679	0.091733	0.9227	1.81	13.5363	0.9903

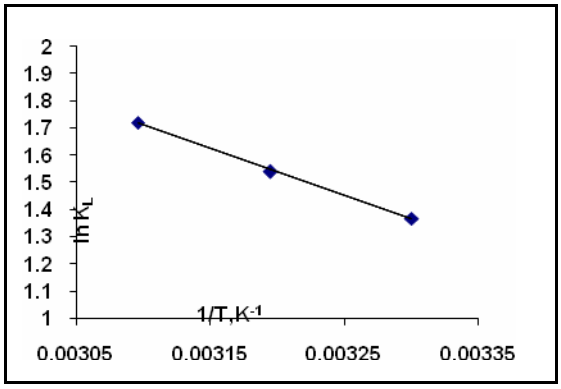
The high correlation coefficient values for DG6 and RO16 related to the Freundlich isotherm showed that this model is suitable to describe the adsorption equilibrium.

Thermodynamic studies

For evaluating the thermodynamic adsorption, the thermodynamic parameters such as Gibbs free energy change of adsorption ΔG°, the enthalpy change of adsorption ΔH° and the entropy change of adsorption ΔS° were calculated using the below equation

$$\ln k_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T}$$

where k_L is the standard thermodynamic equilibrium constant and T is the absolute temperature. The values of ΔH^0, ΔS^0 and ΔG^0 were calculated from the slope and intercept of the plot ln k_L vs 1/T and the results are given in table 4 and in fig.9a & 9b. The Gibbs free energy indicates the degree of spontaneity of the adsorption process of DG6 and RO16 and the higher negative value reports more energetically favourable sorption. The positive values of ΔH° indicate the endothermic nature of the process and the positive value of ΔS° confirms the favourable condition for adsorption of both DG6 and RO16.



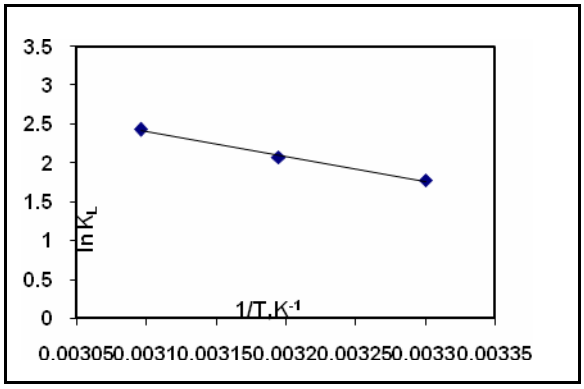


Fig.9a Van't Hoff's plot for the adsorption of DG6

Fig.9b Van't Hoff's plot for the adsorption of RO16

Table 4: Thermodynamic parameters at different temperatures

Dyes	Temp ^{0}C	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 kJ/K/mol
DG6	30	-3.432	14.378	0.05878
	40	-4.020		
	50	-4.607		
RO16	30	-4.251	26.352	0.101
	40	-5.261		
	50	-6.271		

Conclusion

There is a need to enhance the adsorption process effectively by choosing the adsorbent as a cheaper material so as to treat the wastewater in a better way. Thus in the present study, Polyaniline sawdust composite prepared by polymerising aniline on saw dust surface of the fruit of Cordia sebestena via chemical route at room temperature could be used as adsorbent for removing colour of DG6 and RO16 from aqueous solutions. The percentage removal for DG6 was decreased from 78.82% to 72.96% and for RO16, it decreased from 82.33% to 75.48% with an increase in the initial dye concentration from 25 to 100 mg/L with PAn/SD as an adsorbent. The kinetic studies reported that the systems fit to pseudo second order model and the adsorption equilibrium data was in good agreement with Freundlich model for both the dyes. The values of thermodynamic parameters showed the spontaneous and endothermic nature of adsorption process. This study was conducted at laboratory conditions using synthetic dye solution. Hence the results obtained may vary if applied to real samples because the textile industries uses mixture of dyes for various applications. From the results of the present study, it is concluded that PAn/SD was found to be suitable adsorbent for the removal of both direct (DG6) and reactive (RO16) dyes (anionic dyes).

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