Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(2):268-274

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Adsorption of acidic and basic dyes from aqueous solutions using polyaniline coated sawdust as an adsorbent

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ABSTRACT

Polyaniline which is coated onto sawdust prepared from fruit of the gardening plant material Cordia Sebestena is used as an adsorbent (PAn/SD) for removing acidic (Acid Orange 7) and basic (Basic Red 29) dyes from aqueous solutions. Batch mode adsorption study was performed to investigate the effects of the main parameters such as contact time, pH, initial dye concentration and temperature. Using the prepared adsorbent, various kinetic studies and isotherm studies were employed to analyze the feasibility and mechanism of adsorption of both the dyes. The kinetic study obeys pseudo second order and the isotherm study fits with Freundlich model for both acidic and basic dyes. The percentage removal of Acid Orange 7 onto the adsorbent PAn/SD decreases from 87.18% to 78.13% and for Basic Red 29, it decreases from 84.40% to 76.08% with the increase in initial dye concentration from 25 mg/L to 100 mg/L at 30º C. Thermodynamic parameters like ΔGº, ΔHº and ΔSº were also evaluated for both the dyes. It was found that the chemical modification of the fruit of the gardening plant material waste such as sawdust coated onto polyaniline can be used as the best adsorbent for the removal of acidic and basic dyes.

Keywords: Polyaniline coated sawdust, Acid Orange 7, Basic Red 29, Cordia Sebestena, Batch mode adsorption.

INTRODUCTION

Dye pollutants from various industries are an important source of environmental contaminations. Most industries use dyes and pigments to color their products. Perhaps dyes are the serious pollutants of our environment as far as color pollution is concerned. Color affects the nature of water and inhibits the sunlight penetration into the stream and reduces photosynthetic activity. Some of the dyes are carcinogenic and mutagenic. The removal of color from dye-bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. Traditional technologies to treat textile wastewater include various combinations of biological, physical and chemical methods but these methods require high capital and operating costs. Thus, it has become necessary to develop new environmentally friendly ways to clean up contaminants using low-cost methods and materials.

Adsorption has proven advantages over other methods because of simple design and involves low investment [1]. Activated carbon has undoubtedly been the most popular and widely used effective adsorbent for the removal of dye bearing effluents [1] and it remains an expensive material. Therefore, there is a need to look into alternatives to investigate a low cost material, which is effective and economical. So far, many adsorption studies utilizes the plant wastes as adsorbent, the literature is insufficient about the use of polymer coated sawdust as an adsorbent. Thus in this study, an attempt have been made to develop a new low-cost adsorbent using polyaniline coated sawdust (PAn/SD) which is prepared from the fruit of the gardening plant material, Cordia Sebestena, a waste material for the removal of Acid Orange 7 and Basic Red 29 from aqueous solution.

Cordia Sebestena is widely planted throughout the tropics and subtropics as an ornamental plant in gardens because of its flowers. It has dark green, oval shaped leaves, and grows oval shaped fruits. It is commonly known as the Geiger tree. Cordia Sebestena tolerates drought but not frost. The fruit of this plant does not have any economical importance and usually it is not used for edible purpose. It has also been proved to be a good and low-cost precursor material for the development of activated carbon.

In the present study, the effect of contact time, pH, initial dye concentration and temperature on the removal of both the dyes using prepared adsorbent (PAn/SD) was studied. The experimental datas proves that the prepared adsorbent (PAn/SD), polyaniline coated sawdust prepared from the fruit of the gardening plant material Cordia Sebestena can be used as the best effective adsorbent for removing Acid Orange 7 and Basic Red 29 from aqueous solution to a greater extent.

EXPERIMENTAL SECTION

The fruit of Cordia Sebestena is collected from the local area. It is washed several times with water to remove particles and waste adhered on the surface. It is then dried in sunlight for a period of 10 days. The dried material was made into sawdust. Then the sawdust was used for the preparation of the adsorbent.

Adsorbent Preparation

Polyaniline coated sawdust (PAn/SD)

The sawdust was first washed with distilled water in order to remove impurities and finally dried at 333K for 2 hours. In order to prepare polyaniline coated sawdust, 5.0g of sawdust immersed in 50 ml of 0.20M freshly distilled aniline in 1M HCl solution for 6 hours before polymerization. The excess of the monomer solution was removed by simple decantation. Then 50 ml of 0.5M $(NH_4)_2\ S_2\ O_8$ as an oxidant solution was added into the mixture gradually, and the reaction was allowed to continue for 4 hours at room temperature. The polyaniline coated sawdust (PAn/SD) was filtered, washed with distilled water, dried in an oven at about 60 ºC and sieved before use [2]. The characteristics of the PAn/SD were studied as per the standard procedures [3,4] and the surface morphology was analzed by Scanning Electron microscope images.

Adsorbate Preparation

The dyes used in this experiment were acidic and basic dyes. The acidic dye used was Acid Orange 7 which is anionic in nature and the basic dye was Basic Red 29 which is cationic in nature. The characteristics of AO7 and BR29 are given in Table 1.The dyes were used as received from dyeing unit, Erode without further purification. The structures of Acid Orange 7 and Basic Red 29 are presented in Fig.1a & 1b. The stock solutions were prepared by dissolving 1g of dyes in water and upto 1000ml using double distilled water. The concentration of the dyes solution were determined by using UV-Vis spectrophotometer (Elico make BL 198) at their wavelength.

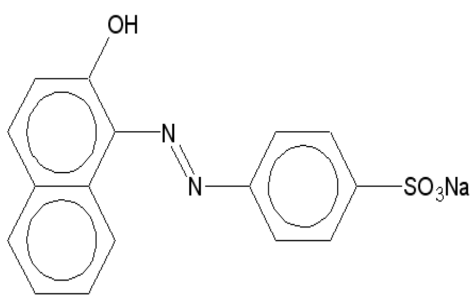

Fig.1a Molecular structure of Acid Orange 7

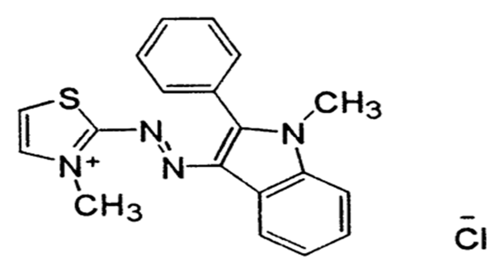

Fig.1b Molecular structure of Basic Red 29

Table 1: Characteristics of AO7 & BR29

Properties	AO7	BR29
CAS No	633-96-5	42373-04-6
C.I NO	15510	11460
Chemical formula	$C_{16}H_{11}N_2NaO_4S$	$C_{19}H_{17}ClN_4S$
Molecular Weight	350.32	368.98
λ_{max}	481 nm	511nm

Characterization studies

Physico-chemical characteristics of polyaniline coated sawdust (PAn/SD) from the fruit of Cordia Sebestena was studied as per the standard testing methods [5,6] and was given in Table 2.

Table.2: Physico- Chemical Characteristics of Adsorbent (PAn/SD)

S.No	Properties	PAn/SD
1	pH	7.56
2	Conductivity, mS cm^{-2}	6.143
3	Volatile matter, %	54.32
4	Methylene Blue value, mg/g	33
5	Iodine Number,mg/g	60

SEM Analysis:

SEM micrographs of PAn/SD is shown in Fig 2. It indicates the formation of the polymer matrix (polyaniline) on the surface of the saw dust.

Batch Adsorption Studies

Batch adsorption studies were carried out by adding a fixed amount of adsorbent (0.1g) containing 100ml of different initial concentrations (25-100mg/L) of dye solutions (AO7 and BR29). At different time intervals, the dye solutions were taken and centrifuged. Absorbance of supernatant solution was noted using spectrophotometer (Elico make: model BL 198) and analyzed for residual dye concentration. The experiments were carried out at different experimental conditions by varying initial dye concentration, contact time, pH and temperature.

pH study of dye adsorption

In order to find out the effect of pH, 0.1g of the adsorbent (PAn/SD) was treated separately with 50ml of 50mg/L of AO7 and BR 29 at pH values from 2 to 11. By adding dilute HCl or NaOH solutions, the pH solution was adjusted in the range of 2 to 11. The experiment was carried out at room temperature and the amount of dyes adsorbed was determined.

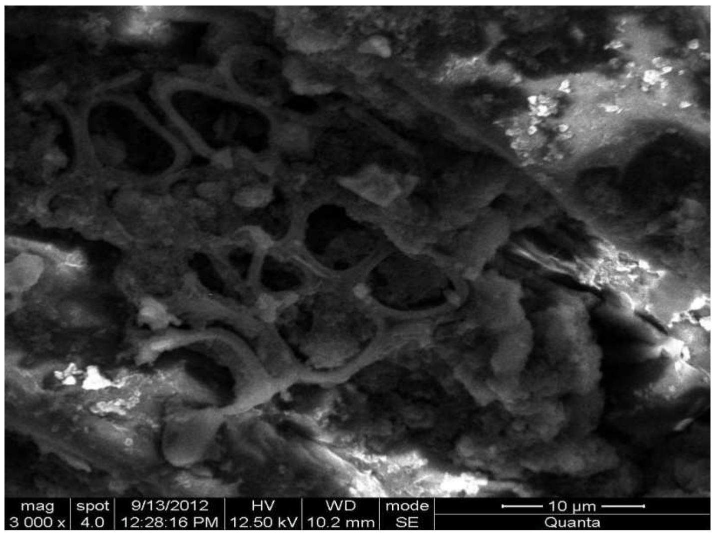

Fig.2 SEM image of PAn/SD

Isotherm study

The study is carried out by taking 0.1g of the adsorbent (PAn/SD) with 100ml of dye solutions separately (AO7 & BR29) with varying concentration in the range 25 – 100mg/L at different temperatures. The amount of dye adsorbed at equilibrium time was measured.

RESULTS AND DISCUSSION

Effect of initial dye concentration and agitation time

Experiments were performed with different initial dye concentrations of both the dyes (AO7 & BR29) ranging from 25 to 100 mg/L to determine the rate of adsorption. In order to carry out this experiment, 0.1g of adsorbent (PAn/SD) was treated with 100ml of 25-100 mg/L of both the dye solutions at its natural pH respectively. The mixture was agitated in a mechanical shaker for different periods of contact time (10-100 min).Results from both the dyes study shows that adsorption process in highly dependent on the initial concentration of the dyes in the solution. The percentage removal of AO7 decreases from 87.18% to 78.13% and for BR 29 decreases from 84.40% to 76.08% as its initial concentration increases from 25 mg/L to 100 mg/L (Fig.3a &3b). However, the total amount of dyes (x/m) uptake is increased gradually. The adsorption capacity at equilibrium increased from 21.80 mg/g to 78.13 mg/g for AO7 and 21.10 mg/g to 76.08 mg/g for BR 29 with an increase in the initial concentrations form 25 to 100 mg/L. This is due to the increase in availability of the dye molecules near adsorbent. Similar results were observed for the adsorptive removal of acid violet 49 by polyaniline coated sawdust [7] and acid blue 92 by Euphorbia Antiquorum L [8].

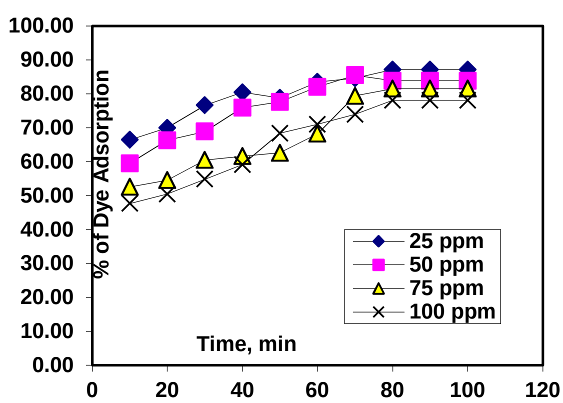

Fig.3a Effect of agitation time on the percentage removal of AO7 dye at 30°C

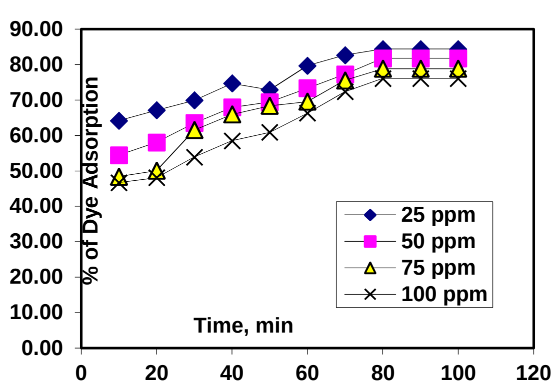

Fig.3b Effect of agitation time on the percentage removal of BR29 dye at 30°C

It was also observed that the rate of removal of AO7 and BR29 dyes increases with an increase in contact time to a certain extent. Both AO7 and BR29 attains maximum percentage removal at 80 minutes. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material.

Similar behavior was reported for the adsorption of acid blue 92 by Euphorbia Antiquorum L[8] and adsorption of basic violet 3 by Euphorbia Tirucalli L [9].

Effect of pH

It is noted that the percentage removal of AO7 was higher when the pH is below 4 (Fig.4). After pH 4, the adsorption rate decreased. The electrostatic attraction between the adsorbent (PAn/SD) and the adsorbate (anionic (AO7) dye) is high in acidic conditions, because the surface of the adsorbent is positively charged due to high concentration of H^+. In the case of BR29, the high percentage removal is observed at the pH range of 9-10 (Fig.4), because at alkaline conditions the surface of the adsorbent become negative so that it enhances the positively charged cationic dyes [10].

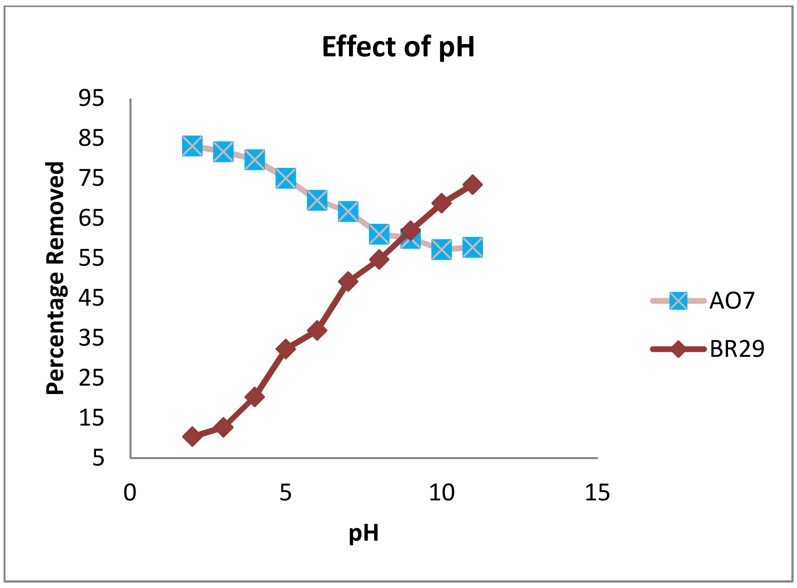

Fig.4 Effect of pH of AO7 & BR29

Effect of temperature

The temperature study was carried at 30^0, 40^0 and 50^0C for both the dyes. It is noted that the percentage removal at equilibrium increases with increasing temperature. The percentage removal at equilibrium increased from 83.90% to 91.85% for AO7 and 81.80% to 86.73% for BR29 at initial concentration of 50mg/L (Fig.5). The increase in uptake with temperature indicates that the sorption of AO7 and BR29 by PAn/SD is endothermic in nature. Similar reports were observed for the adsorption of AG25 by (PAn/SD) [11] and the adsorption of BR29 by EAAC [12].

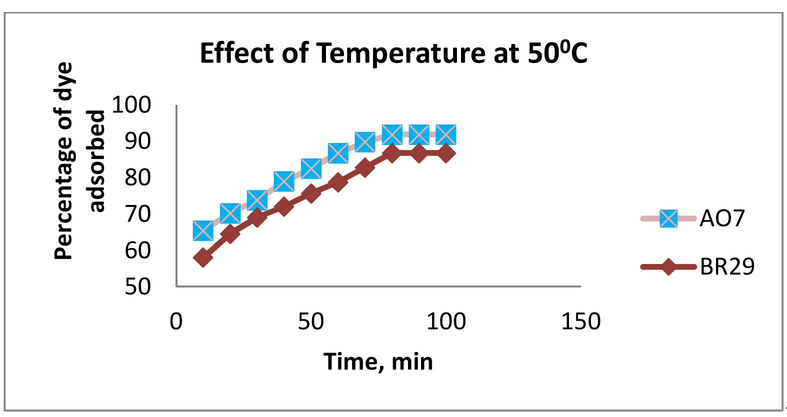

Fig.5 Effect of temperature on the adsorption of AO7 & BR29 dyes at initial concentration of 50mg/L at 50^0C

Adsorption Kinetics

The adsorption of AO7 and BR29 onto PAn/SD were analyzed by pseudo-first order and pseudo second order kinetic models. The integrated linear form of pseudo first order equation [13] is

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)\ t$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at time t (min) and at equilibrium and k_1 is the pseudo –first order rate constant (min $^{-1}$). The value of q_e and k_1 is calculated from intercept and slope of the plot log (q_e-q_t) vs time for different initial concentrations and for different temperatures and the values are given in table 4a & 4b (Fig.6a & 6b and 7a & 7b). From the values of r^2, it is clear that pseudo first order equation does not fit well for both AO7 & BR 29 dyes for the whole range of adsorption process.

The pseudo second order equation[14] is,

$$t/ q_t = 1/ k_2 q_e^2 + t/ q_e$$

where k_2 is the rate constant of pseudo second order adsorption (g/mg min) and q_e is the equilibrium adsorption capacity (mg/g). The value of q_e and k_2 is determined from the intercept and slope of the plot t/q_t vs t for different initial concentrations and for different temperatures and the values are given in table 4a & 4b (Fig.6a & 6b and 7a &

7b). The correlation coefficient values are greater than 0.99 for both AO7 & BR 29 dyes. It shows that the adsorption of AO7 & BR29 by PAn/SD follows the pseudo second order kinetic model. Similar reports were observed for the adsorption of carmosine an anionic dye by (P3MTh/SD) [15] and the adsorption of BV3 by Euphorbia Tirucalli L[9].

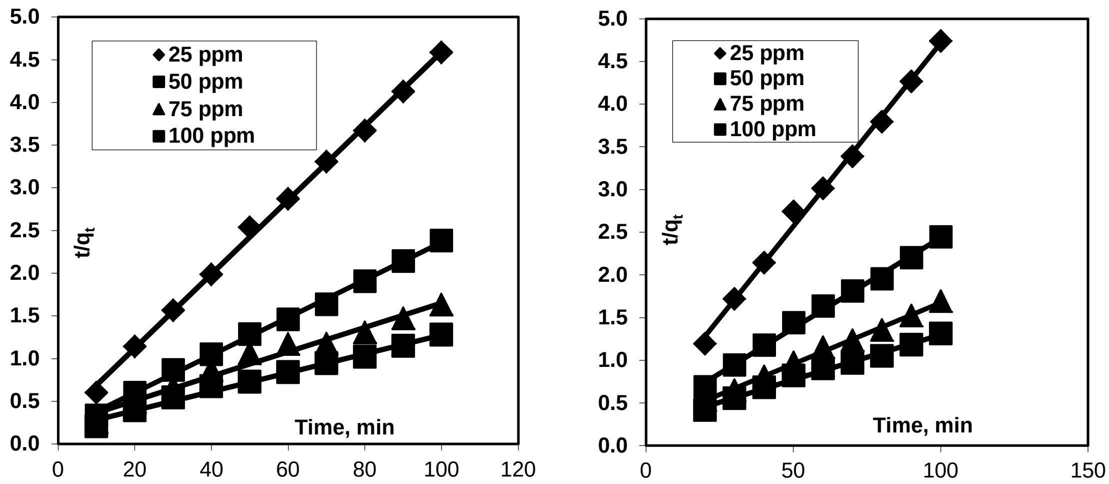

Fig.6a & 6b Pseudo second order plots for the adsorption of AO7 & BR29 dyes at different initial dye concentrations

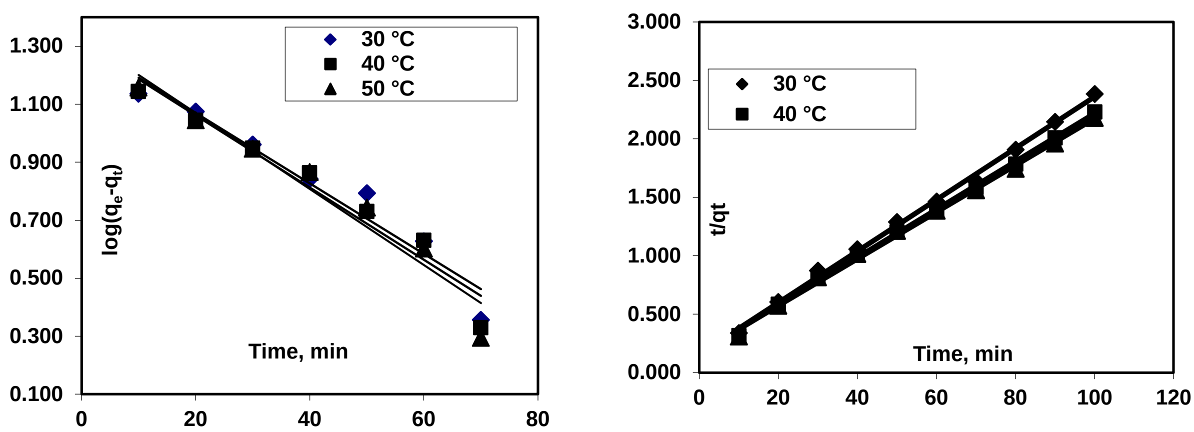

Fig.7a & 7b Pseudo second order plots for the adsorption of AO7 & BR29 dyes at different temperatures

Table 4a: Kinetic Model values for adsorption of AO7 and BR29 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	K2 x 10^{-4} (g/mgmin)	q_e cal(mg/g)	r^2
AO7	25	0.03431	7.820	0.9375	7.43	23.04	0.9984
	50	0.04629	23.290	0.9314	3.07	45.45	0.9974
	75	0.03339	43.003	0.6442	0.92	69.93	0.9713
	100	0.03431	55.055	0.9373	0.71	90.09	0.9878
BR29	25	0.03662	9.66940	0.8227	4.39	23.26	0.9959
	50	0.02810	20.55410	0.9445	1.42	47.17	0.9951
	75	0.03362	37.51450	0.9133	0.84	69.93	0.9961
	100	0.03109	52.13140	0.856	0.46	94.34	0.9897

Table 4b: Kinetic Model values for adsorption of AO7 and BR29 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 x 10^{-4} (g/mgmin)	q_e cal(mg/g)	r^2
AO7	30	0.04629	23.2900	0.9314	3.07	45.45	0.9974
	40	0.04928	29.4640	0.9358	2.62	48.54	0.9981
	50	0.04007	25.7210	0.9149	2.32	50.00	0.9968
BR29	30	0.02810	20.5541	0.9445	1.94	45.25	0.9925
	40	0.02879	20.4785	0.9498	2.05	46.51	0.994
	50	0.03017	21.4880	0.9448	2.05	47.62	0.9947

Adsorption isotherm

The Langmuir [16] and Freundlich [17] models were employed to explain the adsorption of AO7 and BR29 onto PAn/SD. The Langmuir adsorption isotherm is used for monolayer adsorption. It is represented by the equation

$$\frac{1}{q_e} = \frac{1}{kc_e q_m} + \frac{1}{q_m}$$

where q_e is the amount is adsorbed at equilibrium (mg/g), q_m is the monolayer adsorption capacity (mg/g), C_e is the equilibrium concentration of adsorbate (mg/l) and k is the Langmuir constant related to energy of adsorption. The values of q_m and k were calculated from the intercept and slope of the plot C_e/q_e vs C_e and the values are given in table 5. The experimental data does not fit for Langmuir isotherm based on correlation coefficient.

The linear form of Frendlich equation is

$$\log q_e = \log k_f + \left(\frac{1}{n}\right)\log C_e$$

where k_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, q_t is the amount of dye adsorbed per unit mass of adsorbent (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L). The values of k_f and 1/n were calculated from the intercept and slope of the plot log q_e vs log C_e and the values are given in table 5 (Fig.8a & 8b). The 1/n value is below one for both AO7 and BR29 dyes indicating that the adsorption of dyes is favourable. From the data, it is inferred that k_f values increases with increasing temperature. It indicates that the adsorption process is endothermic in nature. The analysis of the correlation coefficients showed that the Freundlich model was found to be more appropriate to describe the adsorption of both AO7 and BR29 dyes onto PAn/SD.

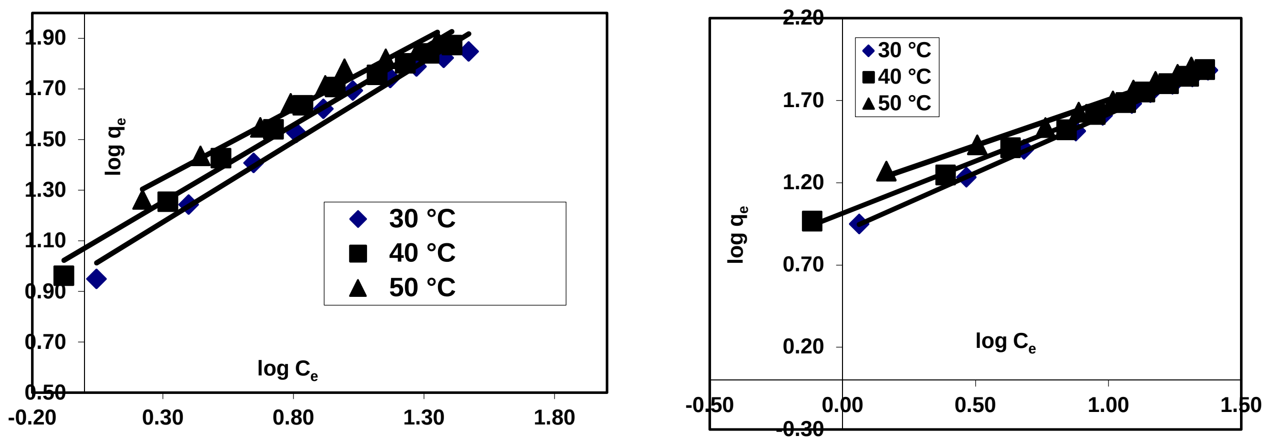

Fig.8a & 8b Freundlich plots for the adsorption of AO7 & BR29 dyes onto PAn/SD

Table 5: Comparison of the coefficients of isotherm parameters of AO7 & BR29

Dyes	Temp ^{0}C	Isotherm models					
		Langmuir			Freundlich		
		q_m (mg/g)	k(L/mg)	r^2	n	k_f ($mg^{1-1/n}L^{1/n}g^{-1}$)	r^2
AO7	30	133.3333	0.056861	0.9753	1.40	8.7599	0.9963
	40	116.2791	0.087935	0.9785	1.52	11.2098	0.9901
	50	106.383	0.124668	0.9741	1.67	14.0023	0.9938
BR29	30	138.8889	0.046875	0.9261	1.39	7.9652	0.9991
	40	107.5269	0.072998	0.8993	1.58	10.3585	0.9974
	50	100	0.123916	0.8900	1.80	14.0799	0.99

Thermodynamics of adsorption

The thermodynamic parameters such as ΔG^o Standard free energy, ΔH^o enthalpy and ΔS^o entropy were calculated from the 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 6. The ΔH^0 value is positive for both AO7 & BR29 dyes which indicates that both the adsorption processes are physical in nature [18]. The enthalpy value ΔH^0 is used to distinguish between chemical and physical adsorption[19,20] . The enthalpy value ΔH^0 for chemical adsorption ranges from 83-830 kJ/mole [21]. The enthalpy value ΔH^0 for AO7 is 22.76 kJ/mol and BR29 is 26.05 kJ/mol which indicates that both the adsorption processes are physical in nature.

Table 6: Thermodynamic parameters at different temperatures

Dyes	Temp ^{0}C	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 kJ/K/mol
AO7	30	-5.0847	22.761	0.0919
	40	-6.0037		
	50	-6.9227		
BR29	30	-4.5743	26.059	0.1011
	40	-5.5853		
	50	-6.5963		

Desorption Studies

Maximum desorption for AO7 is 41.4% and 37.9 % for BR 29 were observed. For AO7, it was observed at a pH range of 9 to 10, and for BR29 it corresponds to 3 to 4. Only a significant amount of dyes (AO7 and BR29) gets desorbed from the dye loaded PAn/SD, because the adsorption process is mainly physical in nature.

CONCLUSION

PAn/SD was easily prepared via direct chemical synthesis on the surface of the sawdust obtained from the fruit of the plant material Cordia Sebestena. The maximum percentage removal was 83.90% for AO7 (Anionic dye) and

81.80% for BR 29 (Cationic dye) by PAn/SD with the initial dye concentration of 50 ppm at 30^0C. The adsorbed amount increased from 21.80 mg/g to 78.13 mg/g for AO7 and 21.10 mg/g to 76.08 mg/g while increasing the initial dye concentration from 25 ppm to 100 ppm. With the increase of temperature from 30^0C to 50^0C, the adsorption of dyes (AO7 and BR29) also increases which indicates that the process is endothermic in nature, which was confirmed by positive ΔH^0 values. The data obtained from kinetic studies revealed that the adsorption of AO7 and BR 29 follows pseudo second order model. Freundlich isotherm model fitted well with the adsorption behavior of both anionic (AO7) and cationic (BR29) dyes. The thermodynamic parameters suggest the spontaneous and endothermic nature of adsorption process. Based on the above study, it can be concluded that the waste fruit material obtained from the plant Cordia Sebestena in which its sawdust is coated with polyaniline called polyaniline coated sawdust (PAn/SD) adsorbent is effective and economically viable for the removal of both anionic (AO7) and cationic (BR 29) dyes.

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