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Comparative Study on Potentiality of Polypyrrole composite as Adsorbent for the removal of Acidic and Basic dyes from Aqueous solutions

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Abstract : The potentiality of polypyrrole coated sawdust (PPy/SD) derived from the fruit of the gardening plant material of Cordia Sebestena to remove acidic dye and basic dye [Acidic Dye namely Acid Orange 7 (AO7) and Basic dye namely Basic Red 29 (BR29)] from aqueous solutions via adsorption was investigated. Adsorption experiments are carried out using batch system in order to do equilibrium adsorption isotherm, kinetics and thermodynamic studies. It is found that chemical modification of plant waste like sawdust coated with polypyrrole called polypyrrole composite is an efficient adsorbent for the removal of AO7 and BR29 from aqueous solutions. Finally, the performance of PPy/SD was compared with both the dyes. The experimental results indicated that adsorbent is effective and economically viable for the removal of both acidic (AO7) and basic (BR29) dyes and is most suitable for the removal of Acid Orange 7 from aqueous solutions than Basic Red 29.

Keywords : Adsorption, Cordia Sebestena, Polypyrrole Coated Sawdust, Acid Orange 7, Basic Red 29.

Introduction

The textile industry uses a variety of chemicals and a large amount of water for all of its manufacturing steps. About 200 L of water are used to produce 1 kg of textile fabric. Thus it generates large volume of wastewater. Hence, surface and groundwater quality gets continuously degraded. It is therefore, the color in wastewater has now been considered as a pollutant that needs to be treated before discharge. Adsorption technique for wastewater treatment has become more popular in recent years owing to their efficiency in the removal of pollutants particularly for removing colour. The most efficient and commonly used adsorbent is commercially activated carbon which is expensive and has regeneration problems. Due to their diversity in surface and porosity, high physical-chemistry stability, regeneration and reuse for continuous process, polymeric adsorbents like polyaniline, polypyrrole, polystyrene, polymaleic anhydride, polymethyl

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methacrylate and their derivatives have been used as alternatives to activated carbon in removal and recovery of organic pollutants from industrial wastewater^{1,2}. In this paper, we have introduced a precursor – fruit of gardening plant material, Cordia Sebestena. Poly pyrrole coated saw dust was chemically synthesized on the sawdust of Cordia Sebestena. The effects of initial dye concentration, agitation time, pH and temperature has been evaluated to assess the possibility of (PPy/SD) for the removal of Acid Orange (AO7) and Basic Red 29 (BR29).

Materials and Methods

Preparation of Polypyrrole coated sawdust PPy/SD

Polypyrrole coated sawdust (PPy/SD) was synthesized on sawdust surface of Cordia Sebestena. In order to prepare polymer coated sawdust, 5.0 g sawdust immersed in 50 ml of 0.2 M freshly distilled pyrrole before polymerization³. The excess of the monomer solution was removed by simple decantation. Then 50 ml of 0.5 M ferric chloride as an oxidant solution was added into the mixture gradually and the reaction was allowed to continue for 4 hours at room temperature. The polypyrrole coated saw dust (PPy/SD) was filtered, washed with distilled water, dried in an oven at about 60⁰C and sieved before use⁴. The coating percentage of each polymer onto sawdust determined by weight difference of the dried saw dust before and after coating and it was nearly 5%⁵.

Preparation of Acid Orange 7 and Basic Red 29 dye solutions

The dyes used for this study are Acid Orange 7, an acidic dye and Basic Red 29, a basic dye. The molecular formula of AO7 is C₁₆H₁₁N₂NaO₄S and its molecular weight is 350.32 g/mol with CI number 15510 and λ_{max} value is 481 nm. The molecular formula of BR29 is C₁₉H₁₇ClN₄S, M.Wt: 368.98 g/mol with CI number 11460, and λ_{max}: 511nm. The dye solutions were prepared by dissolving 1000 mg of the dye in 1 liter double distilled water. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations. The concentration of the dye is determined using Elico make UV-Vis spectrophotometer (BL 198).

The molecular structure of AO7 and BR29 is given in Figure 1 & 2.



Fig.1& 2 Molecular structure of Acid Orange 7(AO7) and Basic Red 29 (BR29)

Batch mode adsorption experiments

Adsorption experiments of Acid Orange (AO7) and Basic Red 29 (BR29) onto PPy/SD are conducted by agitating 100 ml adsorbate solution of known concentration with 0.1 gm of adsorbent. The mixture is agitated in a temperature controlled shaker and samples are withdrawn at different time intervals, centrifuged and analyzed for remaining dye concentration. The unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make UV spectrophotometer (Elico make BL-198) at λ_{max} of 481 nm for AO7 and 511nm for BR29. The effect of pH was studied by using dilute HCl and NaOH solutions. The effect of temperature was studied at three different temperatures (30, 40 and 50⁰C). All experiments were carried out in duplicate and the mean values are reported, where the maximum deviation was within 4%. The effects of each parameter (initial dye concentration, pH, agitation time) were evaluated in an experiment by varying that parameter, while other parameters are maintained as constant. The amount of dyes onto PPy/SD adsorbent were calculated from the following equation⁶.

$$q_t = \frac{C_o - C_e}{M} V$$

where q_t (mg/g) is the amount of dye adsorbed at time t , C_0 and C_t (mg/L) are the concentration of dye at initial and equilibrium respectively. V (L) is the volume of the solution and M (g) is the mass of dry adsorbent used.

Results and Discussion

Effect of Agitation Time and Initial Dye Concentration

In order to determine the rate of adsorption, experiments were conducted at different initial dye concentrations ranging from 25 to 100 mg/L at 30°C. The variation in the percentage removal of AO7 and BR29 with contact time at different initial dye concentrations at 30°C by the adsorbent PPy/SD shows that the percentage of dye removal was decreased from 90.05% to 81.25% for AO7 and from 87.10% to 79.96% for BR29 while increasing the initial dye concentrations from 25 to 100 mg/L. If initial dye concentration is increased, there is an increased competition for the active adsorption sites and the adsorption process will slow down. The adsorption capacity at equilibrium was increased from 22.5 mg/g to 81.25 mg/g for AO7 and from 21.78% mg/g to 79.96% mg/g for BR29 by PPy/SD with an increase in the initial concentrations from 25 to 100 mg/L.

This may be due to the heterogeneity obtained by the presence of functional groups on the surface of the polymer composites⁴. The dye molecules may occupy more sites on the polymer composites due to the orderly arrangement of polymer matrix. It was suggested that the rate of dye removal was high due to the ion exchange mechanism between the oppositely charged functionalities originating from monomer (or oxidant solutions during their synthesis) and the anionic dye molecules⁷.

Effect of pH

pH of a dye solution plays an important role in the adsorption process. The effect of initial pH on the adsorption of AO7 and BR29 onto PPy/SD have been investigated and shown in Fig.3a & 3b. The percentage of AO7 dye adsorption by PPy/SD was maximum at pH 2 and decreased on increasing the pH. It is due to high electrostatic attraction between the positively charged (high concentration of H^+) surface of the adsorbents and anionic dye⁸. When the pH is increased, the electrostatic repulsion increases and the adsorption rate gets decreased. Whereas the maximum percentage removal of BR29 onto PPy/SD occurs at a high pH of 11. Moreover, the electrostatic repulsion between the positively charged BR29 and the surface of adsorbent is lowered at higher pH and consequently, the removal efficiency is increased.

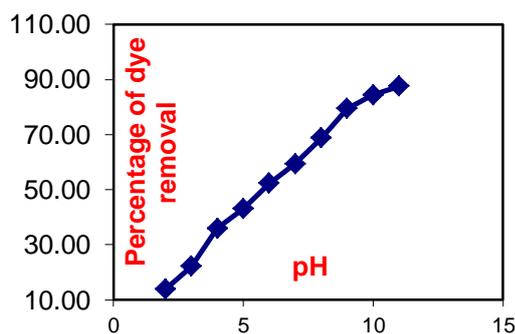
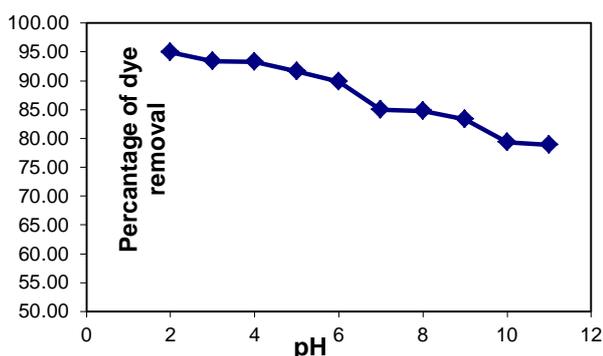


Fig.3a Effect of pH for adsorption of AO7 onto PPy/SD

Fig.3b Effect of pH for adsorption of BR29 onto PPy/SD

Effect of Temperature

The experiments were carried out at three different temperatures (30, 40 and 50°C) to study the effect of temperature on the adsorption of AO7 and BR29 by PPy/SD respectively and the results are shown in Figure 4a and 4b. The percentage removal increased from 89.23% to 94.05% for AO7 and from 84.33% to 89.20% for

BR29 by PPy/SD respectively on increasing the temperature. This indicates that the sorption of acidic dye and basic dye on given polypyrrole coated saw dust of Cordia Sebestena is endothermic process.

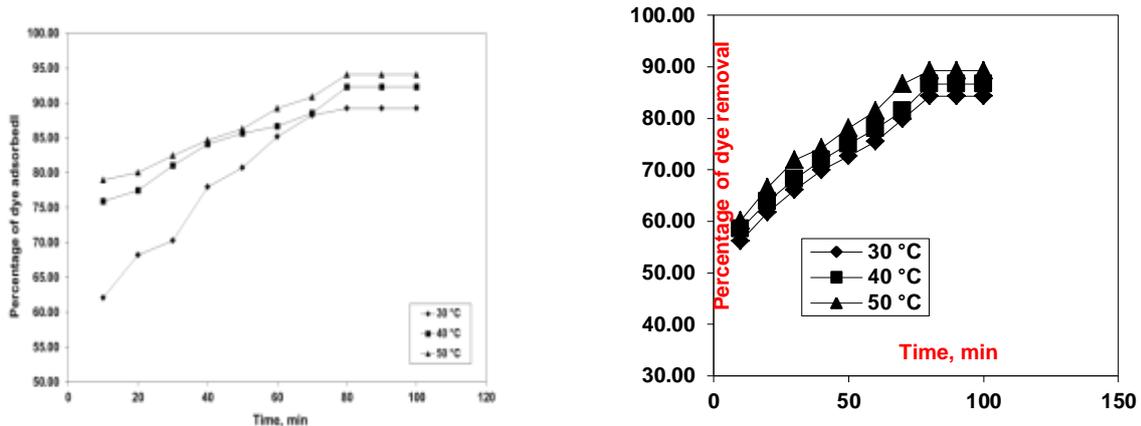


Fig 4a Effect of temperature on the percentage removal of AO-7 dye onto PPy/SD
Fig.4b Effect of temperature on the percentage removal of BR 29 dye onto PPy/SD

Table 1a: Calculated kinetic parameters for the adsorption of AO7 onto PPy/SD at various initial dye concentrations and at various temperatures

Parameter	AO7 onto PPy/SD						
	Initial dye concentration, mg/L				Temperature, °C		
	25	50	75	100	30	40	50
q _e exp.(mg/g)	22.51	44.62	63.28	81.25	44.62	46.15	47.03
Pseudo first order kinetics							
k ₁ x10 ⁻² (min ⁻¹)	3.20	4.97	3.98	3.73	4.97	2.44	2.56
q _e cal.(mg/g)	7.22	32.37	48.37	57.81	32.37	11.33	11.57
r ²	0.978	0.8752	0.7596	0.935	0.8752	0.9854	0.9386
Pseudo second order kinetics							
k ₂ x10 ⁻⁴ (g/mg min)	78.00	23.40	10.20	7.8	23.4	41.00	41.10
h	4.38	5.56	5.26	6.72	5.56	9.58	9.88
q _e cal.(mg/g)	23.70	48.78	71.94	92.59	48.78	48.31	49.02
r ²	0.999	0.9969	0.9879	0.9922	0.9969	0.998	0.9978

Kinetic studies

To evaluate the adsorption kinetics of Acid Orange7 and Basic Red 29, Lagergren first – order and pseudo second order models were used to fit the experimental data.

The first order equation is ⁹

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

Where q_t and q_e are the amount of dye adsorbed (mg/g) at time t(min) and at equilibrium and k₁ is the pseudo – first order rate constant (min⁻¹).

The plot of log (q_e – q_t) versus t should give a straight line with a slope of – k₁/2.303 and intercept log q_e. Calculated values of k₁ and q_e are summarized for the adsorption of AO7 and BR29 onto PPy/SD (figure not shown) at different initial dye concentrations and different temperatures in Table 1a and 1b. The pseudo first – order kinetic model of Lagergren does not fit well with the experimental data over the whole range of initial concentrations studied.

Table 1b: Calculated kinetic parameters for the adsorption of BR29 onto PPy/SD at various initial dye concentrations and at various temperatures

Parameter	BR29 onto PPy/SD						
	Initial dye concentration (mg/L)				Temperature (^o C)		
	25	50	75	100	30	40	50
q_e exp.(mg/g)	21.78	42.17	60.79	79.96	42.17	43.30	44.60
Pseudo first order kinetics							
$k_1 \times 10^{-2}$ (min ⁻¹)	3.52	2.81	3.06	2.62	2.810	2.671	3.524
q_e cal.(mg/g)	9.225	20.634	32.240	48.741	20.6347	19.9067	24.6660
r^2	0.9009	0.9471	0.8841	0.9067	0.9497	0.9722	0.8847
Pseudo second order kinetics							
$k_2 \times 10^{-4}$ (g/mg min)	44.2	14.7	10.7	4.4	19.7	19.9	20.5
h	2.5432	3.4352	5.1020	4.2863	4.2694	4.5188	4.9213
q_e cal.(mg/g)	23.98	48.31	68.97	99.01	46.51	47.62	49.02
r^2	0.9985	0.9952	0.9938	0.9877	0.9933	0.9936	0.9951

The pseudo – second order kinetic equation is expressed as ¹⁰

$$t/q_t = 1/k_2q_e^2 + t/q_e$$

where, k_2 is the rate constant (g/mg min) and q_e is the equilibrium adsorption capacity (mg/g)¹³

The initial adsorption rate, h , (mg/g/min) is expressed as $h = k_2q_e^2$. Figure 5a & 5b show the pseudo second order plots for the adsorption of AO7 onto PPy/SD respectively at various initial dye concentrations and at various temperatures. Figure 6a & 6b show the pseudo second order plots for the adsorption of BR29 onto PPy/SD respectively at various initial dye concentrations and at various temperatures. The value of k_2 and q_e determined from the intercept and slope of the plot.

The rate constant k_2 decreases with increase in initial dye concentration and increases with increase in temperature. From the results given in Table 1a & 1b, the adsorption of AO7 and BR29 at different initial dye concentrations and temperatures for PPy/SD fits well to the pseudo second order kinetic model with high correlation coefficient.

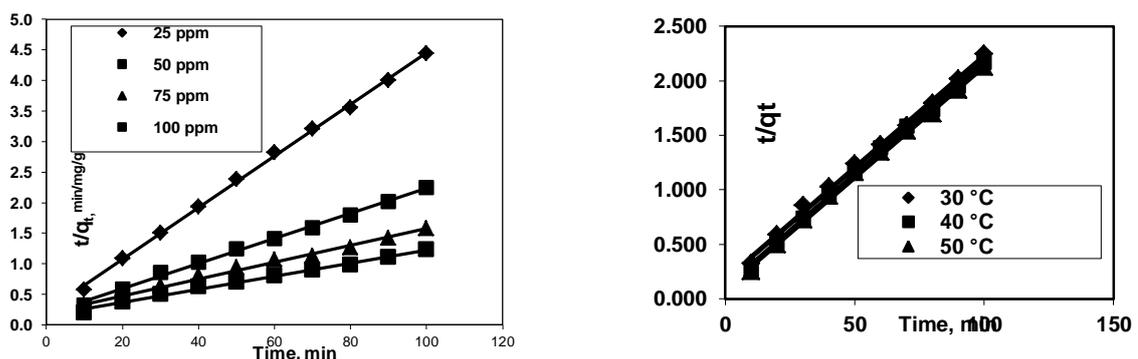


Fig 5a & 5b Pseudo second order plot for the adsorption of AO7 onto PPy/SD at various initial dye concentrations and at various temperatures

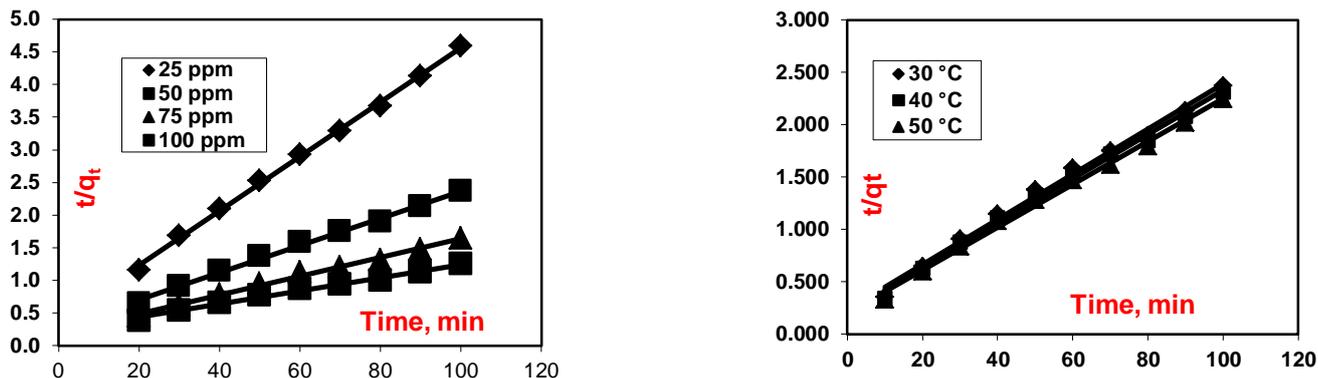


Fig 6a & 6b Pseudo second order plot for the adsorption of BR 29 onto PPy/SD at various initial dye concentrations and at various temperatures

Adsorption Isotherms

To study the adsorption isotherm, the experimental data are interpreted using the two equilibrium models: the Freundlich and the Langmuir equations.

Freundlich isotherm

The Freundlich model¹¹ is employed to describe the heterogeneous system, which is characterized by heterogeneity factor $1/n$ and it considers a multilayer adsorption. The Freundlich isotherm is expressed as

$$\log q_e = \log K_f + 1/n \log C_e$$

where K_f & $1/n$ 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 $\log C_e$.

The r^2 value for Langmuir isotherm is 0.9045 for BR29 onto **PPy/SD** obviously lower than the Freundlich isotherm which is 0.9946. From the Table 2, it is concluded that the adsorption of BR29 onto **PPy/SD** match Freundlich isotherm model. Thus Freundlich Zmodel is more appropriate to explain the nature of adsorption rather Langmuir model for BR29 that shows poor fit (Fig 7b).

Langmuir isotherm

Langmuir model suggests a mono layer sorption and uniform energies of adsorption onto the surface, without interaction between the sorbed molecules¹².

Table 2: Results of isotherm plots for the adsorption of AO7 and BR29 onto PPy/SD

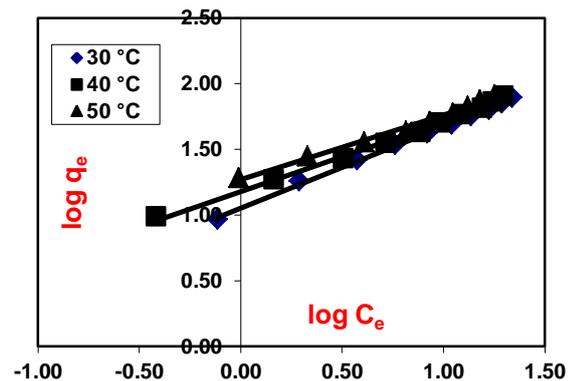
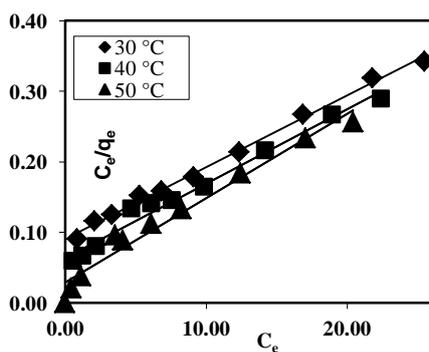
Parameter	AO7 onto PPy/SD			BR29 onto PPy/SD		
	Temperature (°C)			Temperature, °C		
	30	40	50	30	40	50
Freundlich Isotherm						
n	1.65	1.82	2.76	1.62	1.89	2.03
k _f (mg ^{1-1/n} L ^{1/n} g ⁻¹)	11.83	15.58	26.84	11.3553	15.1390	18.6080
r ²	0.9759	0.9763	0.9818	0.9981	0.9953	0.9903
Langmuir Isotherm						
Q ₀ (mg/g)	98.04	95.24	83.33	108.6957	90.9090	90.0900
b _L (L/mg)	0.1125	0.1654	0.4167	0.0883	0.1306	1.2293
r ²	0.9954	0.9834	0.9666	0.9369	0.8900	0.8866

The linear form of Langmuir is expressed as

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

where q_e is the amount of dye sorbed (mg/g), C_e is the equilibrium concentration (mg/L), q_m is the maximum adsorption capacity for a complete monolayer (mg/g), and K is the sorption equilibrium constant related to the energy of adsorption (L/mg). A plot of $1/q_e$ versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(Kc_e q_m)$.

The results of Langmuir plot are given in Table 2. In case of AO7, the values of adsorption capacity varies from 98.04 to 83.33 mg/g with the increase of temperature from 30°C to 50°C. Langmuir model is more appropriate to explain the nature of adsorption of AO7 with correlation coefficients of 0.9954 to 0.9666 for PPy/SD (Fig.7a).

**Fig.7a Langmuir plot for the adsorption of AO7 dye onto PPy/SD****Fig. 7b Freundlich plot for the adsorption of BR29 dye onto PPy/SD**

Thermodynamic studies

Thermodynamic parameters like ΔH^0 , ΔS^0 and ΔG^0 were measured based on Van't Hoff's plot.

$$\ln K_L = \Delta S^0 / R - (\Delta H^0 / R) \cdot 1/T$$

where, k_L is the Langmuir equilibrium constant, ΔH^0 & ΔS^0 are the standard enthalpy and entropy changes of adsorption respectively and the values of ΔH^0 and ΔS^0 are calculated from the slopes and intercepts of the linear plot of $\ln k_L$ vs $1/T$. The free energy of specific adsorption ΔG^0 (kJ/mol) is calculated from the following equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

The thermodynamical parameters calculated from Eyring's plot are given in Table 3. Negative standard free energy of adsorption indicates that the adsorption process is favorable and spontaneous in nature. The endothermic nature of adsorption is confirmed by the positive ΔH^0 value. Positive values of ΔS^0 suggested good affinity of the dye towards the adsorbent and the adsorption is spontaneous in nature¹³.

Table 3: Thermodynamic parameters for the adsorption of AO7 and BR29 onto PPy/SD

Temperature °C	AO7 onto PPy/SD			BR29 onto PPy/SD		
	ΔH^0 kJ/mol	ΔS^0 KJ/K/mol	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 J/K/mol	ΔG^0 kJ/mol
30	46.46	0.1726	-5.8378	30.99	0.1206	-5.5518
40			-7.5638			-6.7578
50			-9.2898			-7.9638

Conclusion

PPy/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 81.25% for AO7 (Acidic dye) and 79.96% for BR29 (Basic dye) by PPy/SD while increasing the initial dye concentrations from 25 to 100 mg/L. With the increase of temperature from 30°C to 50°C, 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 BR29 dye whereas Langmuir model is more appropriate to explain the nature of adsorption of AO7 dye with high correlation coefficient values. 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 polypyrrole called PPy/SD adsorbent is effective and economically viable for the removal of both acidic (AO7) and basic (BR 29) dyes and is most suitable for the removal of Acid Orange 7 from aqueous solutions than Basic Red 29 based on its percentage removal.

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