Application of Activated Carbon and Polypyrrole Coated Sawdust for Adsorption of Acidic Dye from Aqueous Solutions: A Comparative Study

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Decolorization of textile effluents using the conventional technologies is not effective because of their limitations. A search is required for more effective and economic treatment techniques. Hence the potentiality of activated carbon (CSAC) and polypyrrole coated sawdust (PPy/SD) derived from the fruit of the gardening plant material of *Cordia sebestena* to remove acid orange 7 from aqueous solutions *via* adsorption was investigated. The batch mode adsorption studies were carried out by varying experimental parameters such as pH, initial dye concentration, contact time and temperature. The kinetic data at different concentrations at different temperatures were analyzed for both the adsorbents using pseudo first order and pseudo second order models. The equilibrium data were also analyzed by Freundlich and Langmuir models. Thermodynamic studies were also evaluated. Finally, the performance of CSAC was compared with PPy/SD. The experimental results indicated that polypyrrole coated sawdust (PPy/SD) is most suitable for the removal of acid orange 7 from aqueous solutions than activated carbon (CSAC).

Keywords: Adsorption, *Cordia sebestena*, Activated carbon, Polypyrrole coated sawdust, Acid orange 7.

INTRODUCTION

Among the various known forms of pollution, water pollution is of great concern since water is very much essential for maintenance and survival of all living organisms on earth. Now a day's, water is getting polluted mainly due to dyes discharged from textile industries. Decolorization of textile effluents using the conventional technologies is not effective because of their limitations[1]. A search is required for more effective and economic treatment techniques. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available[2-5]. Conducting polymers such as polypyrrole coated on saw dust are recently used as novel adsorbents due to their electrical conductivity and electronegativity[6]. In this paper, we have introduced a precursor-fruit of gardening plant material *i.e.*, *Cordia sebestena*. The activated carbon was prepared by carbonization followed by chemical impregnation with H_3PO_4. Also poly pyrrole coated saw dust was chemically synthesized on the sawdust of *Cordia sebestena*. Both the adsorbents CSAC and PPy/SD has been tested and made a comparative study to evaluate its potential for the removal of acid orange 7 from aqueous solutions by batch mode adsorption tests.

EXPERIMENTAL

Preparation of activated carbon (CASC): The fruit of *Cordia sebestena* which is considered as waste was dried in sunlight for 10 days. Material was soaked in a boiling solution of 10 % H_3PO_4 for 2 h and kept at room temperature for 24 h. At the end of 24 h, the excess solution was decanted off, the material was air dried and carbonized in muffle furnace at 400 ºC for 0.5 h. The carbon was powdered and activated in a muffle furnace at 800 ºC for a period of 10 min. Then the carbon was washed with plenty of water to remove residual acid, dried and powdered. The surface morphology of CASC visualized *via* scanning electron microscope (SEM).

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 g sawdust immersed in 50 mL of 0.2 M freshly distilled pyrrole before polymerization 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 h at room temperature. The poly-pyrrole coated saw dust (PPy/SD) was filtered, washed with

2814 Geetha *et al.*

distilled water, dried in an oven at about 60 ºC and sieved before use[7]. 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 %[8].

Preparation of acid orange 7 dye solution: The dye used for this study is acid orange 7, an acidic dye. The molecular formula of acid orange 7 is $C_{16}H_{11}N_2NaO_4S$ and its molecular weight is 350.32 g/mol with CI number 15510. Its λ_{max} value is 481 nm. The dye solution was prepared by dissolving 1000 mg of the dye in 1 L double distilled water. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations. The molecular structure of acid orange 7 is given in Fig. 1.
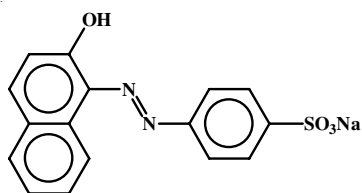
Fig. 1. Molecular structure of acid orange 7

Batch mode adsorption experiments: The adsorption experiments were carried out by agitating 100 mg adsorbent with 100 mL of dye solutions of 25-100 mg/L concentration at 180 rpm on an Orbital Shaker (REMI make). The mixture was withdrawn at specified intervals, centrifuged using electrical centrifuge (Universal make) at 5000 rpm for 10 min and unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make UV spectrophotometer (BL 198) at λ_{max} of 481 nm. 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 50 ºC). 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 dye on CSAC and PPy/SD adsorbent were calculated from the following equation

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

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.

Desorption study: Desorption study helps to elucidate the nature of adsorption and the possibility of recycling the used adsorbent and adsorbate. For performing this experiment, the supernatant was separated after centrifugation and the adsorbent was separated and allowed to agitate with 100 mL of distilled water at the natural pH value above the equilibrium time of adsorption. The desorbed dye solution was estimated as given in the adsorption studies[9].

RESULTS AND DISCUSSION

Characterization studies: SEM micrographs of CSAC and PPy/SD are shown in Fig. 2a,b. Fig. 2a indicates the SEM

micrograph of CSAC showed rough areas on the surface of the carbon and Fig. 2b indicates the SEM micrograph of PPy/ SD showed the formation of the polymer matrix on the surface of the saw dust.
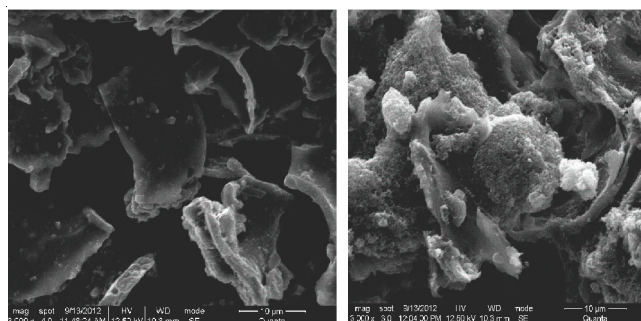

Fig. 2. (a) SEM image of CSAC (b) SEM image of PPy/SD

Effect of agitation time and initial dye concentration: The rate of adsorption is a function of the initial dye concentration and contact time which is an important factor for the effective adsorption. 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 ºC. The variation in the percentage removal of acid orange 7 with contact time at different initial dye concentrations at 30 ºC by both the adsorbents CSAC and PPY/SD are shown in Fig. 3a,b. The percentage of dye removal was decreased from 69.82 to 53.19 % for CSAC and 90.05 to 81.25 % for PPy/SD 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
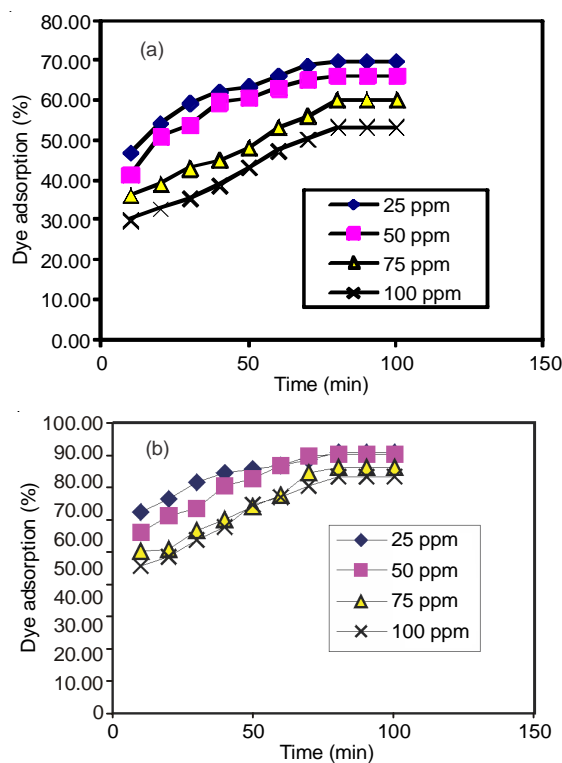

Fig. 3. (a) Effect of agitation time on the percentage removal of acid orange 7 on CSAC at 30 ºC. (b) Effect of agitation time on the percentage removal of acid orange 7 on PPy/SD at 30 ºC

process will slow down. The adsorption capacity at equilibrium was increased from 17.45 to 53.19 mg/g for CSAC and 22.5 to 81.25 mg/g for PPy/SD with an increase in the initial concentrations from 25 to 100 mg/L. This is due to the increase in availability of the dye molecules near adsorbent. Similar behaviours were reported for the adsorptive removal of direct yellow 86 and direct red 224 on carbon nanotubes[10].

The amount of acid orange 7 removal by the CSAC is less than that of PPy/SD. This may be due to the heterogenity obtained by the presence of functional groups on the surface of the polymer composites[7]. The pores on the surface of activated carbon may not be fully occupied by dye molecules where as the dye molecules may occupy more sites on the polymer composites due to the orderly arrangement of polymer matrix. The same result was obtained by our research group for the adsorption of direct blue 71 by activated carbon and polymer composite prepared from *Thevetia peruviana* and the same reason was also reported[11]. 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 molecules[6].

Effect of temperature: The experiments were carried out at three different temperatures (30, 40 and 50 ºC) to study the effect of temperature on the adsorption of acid orange 7 by CSAC and PPy/SD, respectively and the results are shown in Fig. 4a,b. The percentage removal of acid orange 7 increased from 72.14-76.27 % on CSAC and 89.23-94.05 % on PPY/SD, respectively on increasing the temperature. This indicates that the sorption of acidic dye on given activated carbon and polypyrrole coated saw dust of *Cordia sebestena* is endo-thermic process.
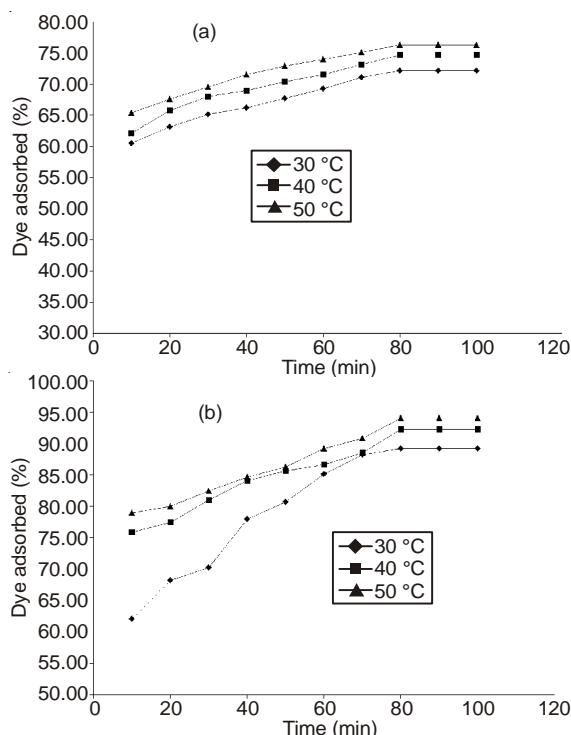

Fig. 4. (a) Effect of temperature on the adsorption of acid orange 7 onto CSAC at initial concentration of 50 mg/L, (b) Effect of temperature on the adsorption of acid orange 7 onto PPy/SD at initial concentration of 50 mg/L

Effect of pH: The percentage of dye adsorption by activated carbon was maximum at pH 6 and decrcased on increasing the pH after 6. While for polypyrrole coated saw dust, it was maximum at pH 2 and decreased on increasing the pH and the results are shown in Fig. 5. It is due to high electrostatic attraction between the positively charged (high concentration of H⁺) surface of the adsorbents and anionic dye[12]. When the pH is increased, the electrostatic repulsion increases and the adsorption rate gets decreased.
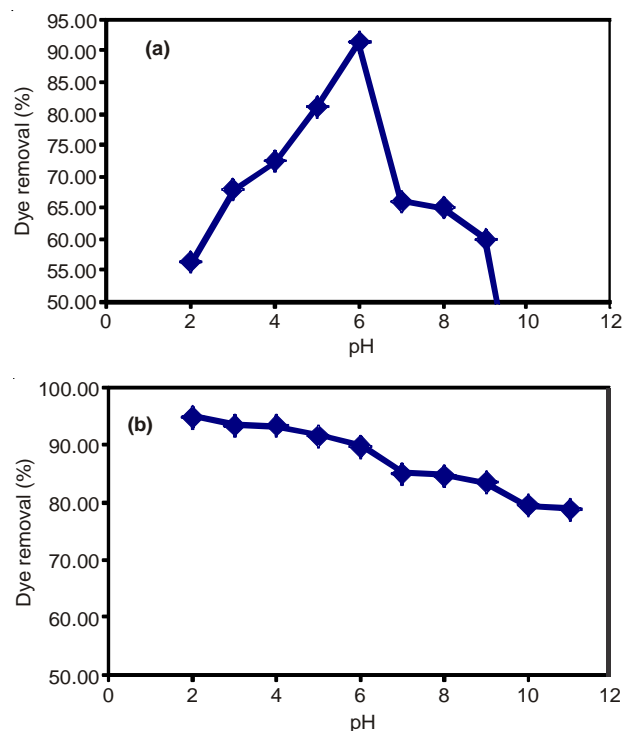

Fig. 5. (a) Effect of pH on CSAC, (b) Effect of pH on PPy/SD

Kinetic studies: To evaluate the adsorption kinetics of acid orange 7, Lagergren first-order and pseudo second order models were used to fit the experimental data. The first order equation is

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$

where q_t and q_e 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 plot of log $(q_e - q_t)$ *versus* t should give a straight line with a slope of $- k_1/2.303$ and intercept log q_e Calculated values of k_1 and q_e are summarized for the adsorption of acid orange 7 on CSAC and PPy/SD (figure not shown) at different initial dye concentrations and different temperatures in Table-1a,b. Similar results were observed for the adsorption of Direct blue 71 by activated carbon and polymer composite prepared from *Thevetia peruviana*[11]. The pseudo first-order kinetic model of Lagergren does not fit well with the experimental data over the whole range of initial concentrations studied.

The pseudo-second order kinetic equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

TABLE-1a							
	CSAC						
Parameter	**Initial dye concentration (mg/L)**				**Temperature (ºC)**		
	25	50	75	100	30	40	50
q_e exp. (mg/g)	17.45	33.10	45.08	53.19	36.07	37.34	38.13
Pseudo first order kinetics							
$k_1 \times 10^{-2}$ (min^{-1})	4.49	4.84	2.86	3.36	3.57	3.15	3.57
q_e cal.(mg/g)	10.35	22.95	28.76	42.18	9.95	8.99	8.97
r^2	0.9222	0.9484	0.9107	0.8985	0.8937	0.9519	0.9717
Pseudo second order kinetics							
$k_2 \times 10^{-4}$ (g/mg min)	68.3	31.7	11.7	8.2	66.1	66.5	75.5
h	2.43	4.16	3.16	3.29	9.2678	9.9900	11.7096
q_e cal. (mg/g)	18.87	36.23	52.08	63.29	37.45	38.76	39.37
r^2	0.9988	0.999	0.983	0.9805	0.999	0.9992	0.9995
TABLE-1b							
	PPy/SD						
Parameter	**Initial dye concentration (mg/L)**				**Temperature (ºC)**		
	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							
$k_1 \times 10^{-2}$ (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	0.9788	0.8752	0.7596	0.935	0.8752	0.9854	0.9386
Pseudo second order kinetics							
$k_2 \times 10^{-4}$ (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

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 $h = k_2 q_e^2$. Fig. 6a,b show the pseudo second order plots for the adsorption of acid orange 7 on CSAC and PPy/SD, respectively at various initial dye concentrations at 30 ºC. Fig. 7a,b show the pseudo second order plots for the adsorption of acid orange 7 on CSAC and PPy/SD, respectively 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,b, the adsorption of acid orange 7 at different initial dye concentrations and temperatures for both CSAC and PPy/SD fits well to the pseudo second order kinetic model with high correlation coefficient.

Isotherm studies: The equilibrium adsorption isotherm is fundamental in describing the interactive behaviour 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 Langmuir[14] and Freundlich[15] models were used to describe the adsorption of acid orange 7 on to CSAC and PPy/SD.

The Langmuir equation can be written as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0}$$

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. The values of Q_0 and b_L calculated from the slopes and interepts of the linear
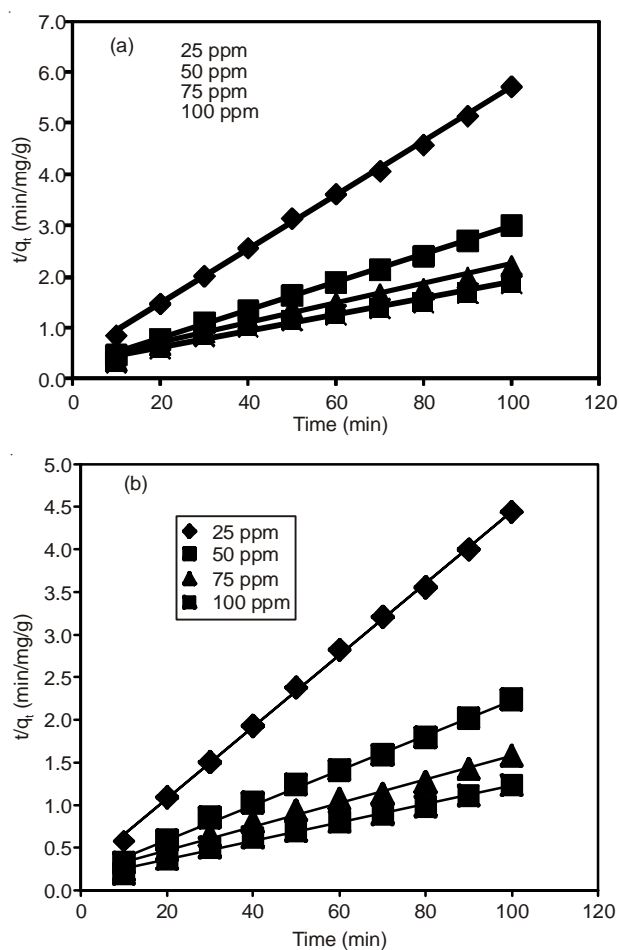

Fig. 6. (a) Pseudo second order plots for the adsorption of acid orange 7 onto CSAC at 30º. (b) Pseudo second order plots for the adsorption of acid orange 7 onto PPy/SD at 30 ºC
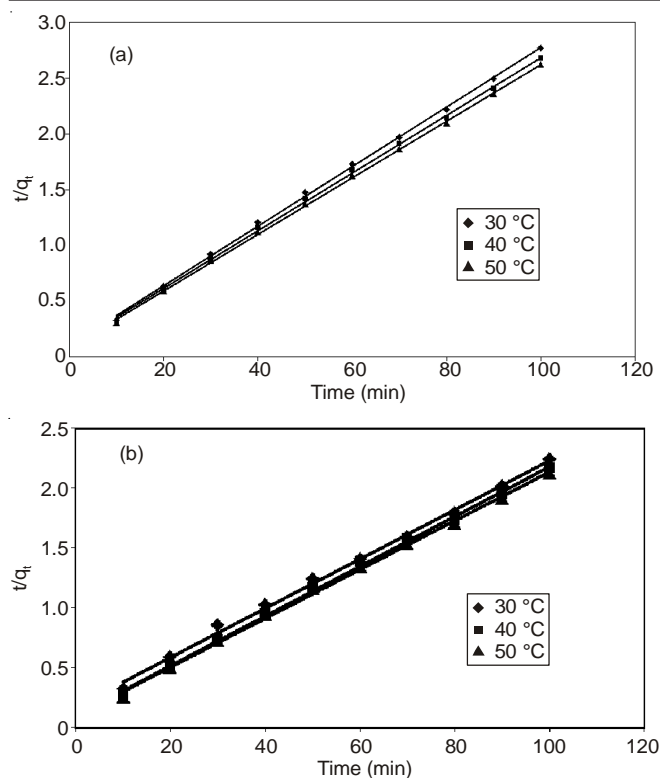
Fig. 7. (a) Pseudo second order plots for the adsorption of acid orange 7 onto CSAC at different temperatures. (b) Pseudo second order plots for the adsorption of acid orange 7 onto PPy/SD at different temperatures
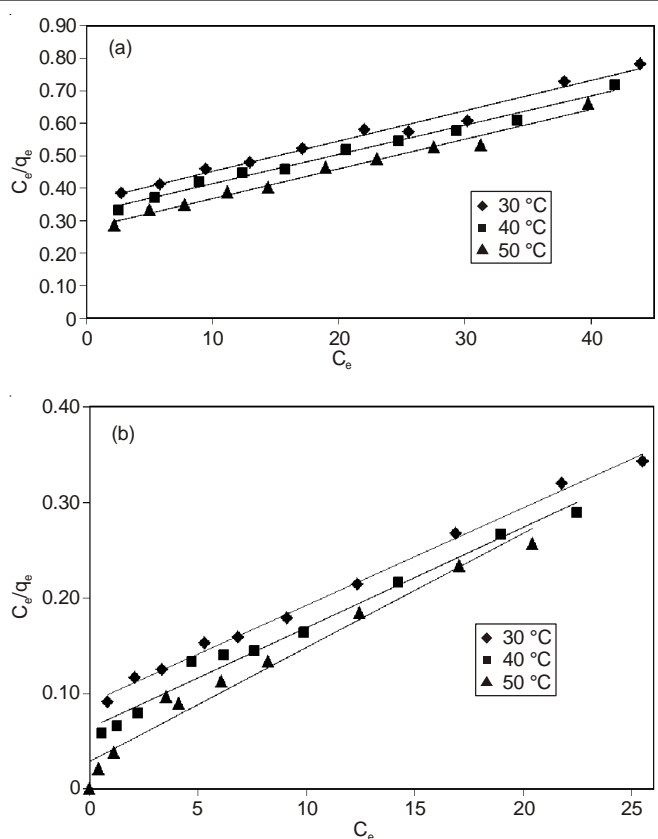

Fig. 8. (a) Langmuir plot for the adsorption of acid orange 7 onto CSAC. (b) Langmuir plot for the adsorption of acid orange 7 onto PPy/SD

plots of C_e/q_e vs. C_e as shown in Fig. 8a,b and the results are summarized in Table-2.

The values of adsorption capacity of CSAC varies between 106.38-111.111 mg/g with the range of temperatures studied (30-50 ºC). In case of PPy/SD, the values of adsorption capacity varies from 98.04 to 83.33 mg/g with the increase of temperature from 30-50 ºC. The high adsorption capacity is due to high surface area and porosity of the adsorbent. The adsorption capacity is comparable with the results reported by the earlier researcher[16,17]. The adsorption energy b_L increases with increasing the temperature for both CSAC and PPy/SD suggested that the maximum adsorption corresponds to a saturated monolayer of dye molecules on all the adsorbents. Further it confirms the endothermic nature of process involved in the system[18].

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L[19] that is defined by the following equation

$$R_L = \frac{1}{(1 + b_L C_o)}$$

where C_o is the initial concentration of dye (mg/L), b_L is the Langmuir constant, R_L value indicated the type of adsorption isotherm to be either unfavourable ($R_L > 1$), favorable ($R_L < 1$) linear ($R_L = 1$) or irreversible ($R_L = 0$). The R_L value ranges from 0.276 to 0.232 for CSAC and 0.082 to 0.023 for PPy/SD for the range of temperatures studied. The R_L value between 0 and 1 indicate favourable adsorption.

Langmuir model is more appropriate to explain the nature of adsorption of acid orange 7 with correlation coefficients of 0.9954-0.9666 for PPy/SD. But in case of CSAC, there is no considerable difference between R^2 values obtained for Langmuir isotherm (about 0.9848) and Freundlich isotherm (about 0.9905). From the high adsorption capacity values of CSAC, it is concluded that it is also better fit with the Langmuir isotherm.

Parameter	CSAC			PPy/SD		
	Temperature (ºC)			Temperature (ºC)		
	30	40	50	30	40	50
Freundlich isotherm						
n	1.34	1.35	1.37	1.65	1.82	2.76
k_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	3.70	4.09	4.71	11.83	15.58	26.84
r^2	0.9888	0.9926	0.9903	0.9759	0.9763	0.9818
Langmuir isotherm						
Q_0 (mg/g)	106.38	111.111	108.695	98.04	95.24	83.33
b_L (L/mg)	0.0262	0.0275	0.0331	0.1125	0.1654	0.4167
r^2	0.9835	0.9870	0.9838	0.9954	0.9834	0.9666

TABLE-2

Temperature (ºC)	CSAC			PPY/SD		
	ΔH° (kJ/mol)	ΔS° (KJ/K/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)	ΔG° (kJ/mol)
30			-2.5265			-5.8378
40	10.351	0.0425	-2.9515	46.46	0.1726	-7.5638
50			-3.3765			-9.2898

TABLE-3

The Freundlich model is employed to describe the heterogeneous system, which is characterized by hetergencity factor l/n and it is considers a multilayer adsorption. The Freundlich isotherm is expressed as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

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 acid orange 7 studied for both CSAC and PPy/SD indicating that the adsorption of dyes is favorable. The results of isotherms are summarized in Table-3.

The 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 apporiate to explain the adsorption of acid orange 7 onto CSAC and PPy/SD.

Thermodynamic studies: Thermodynamic parameters like ΔH°, ΔS° and ΔG° were measured based on van't Hoffs plot.

$$\ln k_L = \frac{\Delta S^\circ}{R} - \left(\frac{\Delta H^\circ}{R}\right) \cdot \frac{1}{T}$$

where, k_L is the Langmuir equilibrium constant, ΔH° and ΔS° are the standard enthalpy and entropy changes of adsorption, respectively and the values of ΔH° and ΔS° 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° (kJ/mol) is calculated from the following equation

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

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° value. Positive values of ΔS° suggested good affinity of the dye towards the adsorbent and the adsorption is spontaneous in nature[20].

Desorption studies: The desorption of dyes by water indicates that the dyes are adsorbed onto CSAC and PPy/SD by physisorption. Maximum desorption of acid orange 7 is 34.7 % for CSAC and 46.2 % for PPy/SD. There is only considerable amount of desorption takes place in both the cases.

Conclusion

In the present study, activated carbon (CSAC) and polypyrrole coated saw dust (PPy/SD) were prepared from the fruit of the gardening plant material *Cordia sebestena* for the adsorption of acid orange 7 from its aqueous solution. The amount of acid orange 7 adsorption increased from 17.45-53.19 mg/g for CSAC and from 22.51-81.25 mg/g for PPy/SD with an increase in the initial concentrations from 25-100 mg/L. Kinetic studies showed that adsorption of acid orange 7 followed pseudo second order kinetic model. The data obtained from adsorption isotherms are well hold with Langmuir model which suggests the monolayer coverage of the dye on surface of CSAC and PPy/SD. The negative ΔG° values obtained from Van't Hoff plots confirm that the adsorption of acid orange 7 by these adsorbents is spontaneous in nature. The positive ΔH° values suggest that the adsorptions of the acidic dye on CSAC and PPy/SD are endothermic in nature. From the kinetic and thermodynamic analyses, it was suggested that the polypyrrole coated saw dust PPy/SD is having the high removal capacity for the removal of acidic dye acid orange 7 compared to the activated carbon CSAC.

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