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Studies on adsorptive removal of Direct Green 6 using a non-conventional activated carbon and polypyrrole composite

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ABSTRACT

Application of activated carbon (CSAC) and polypyrrole composite (PPC) developed from the precursor, fruit of the gardening plant material *Cordia sebestena* has been investigated for the removal of Direct Green 6 (DG6) from aqueous solution. Batch adsorption experiments were carried out using CSAC and PPC and a comparative study was also made. Effect of parameters, namely initial dye concentration, contact time, pH and temperature was studied. The kinetic studies were analysed with pseudo-first-order and pseudo-second-order models. Experimental isotherm data were also analysed with Langmuir and Freundlich adsorption isotherm models. Thermodynamic parameters were also measured. Experimental results showed that percentage removal of DG6 was higher with PPC than the percentage removal obtained by CSAC. Hence, it is proposed that PPC is superior and efficient adsorbent for the removal of DG6 from aqueous solutions.

Keywords: *Cordia sebestena*; Activated carbon; Polypyrrole composite; Direct Green 6; Batch adsorption study

1. Introduction

The presence of dyes in wastewater is undesirable because of the toxicological impact of its entrance into the food chain. The wastewater from dyeing industries is released into nearby land or rivers without any treatment, because the conventional treatment methods are not cost effective in the Indian conditions [1]. Furthermore, dyes in wastewater are difficult to remove because they are stable to light, heat and oxidizing agents. In short, they are not easily degradable [2–6].

Thus, the removal of dyes from coloured effluents is one of the major environmental problems. Number of various technologies has been used for the treatment of colour removal from dyeing effluent. But adsorption is one of the most effective methods and activated carbon (CSAC) is the most widely used adsorbent to treat the various kinds of dyes containing wastewater, recognizing the economic drawback of commercial CSAC [7,8]. The above reasons have induced high research interest in the use of agricultural waste as starting materials because of their low cost and widespread availability.

Recently, there have been several reports of the economic removal of dyes using different adsorbents such as rice husk, cotton, bark, hair and coal [9], perlite [10], sewage sludge-based CSACs [11], CSAC [12–14], apple pomace and wheat straw [15], banana and orange peel

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[16], orange bentonite [17], pearl millet husk [18], peat particles [19], wood [20], flyash and coal [21]. Nowadays sawdust derived from waste plant material which is coated with polymer called polymer composite has received particular attention as an economical adsorbent for removing colour from dyes containing wastewater.

In the present study, the fruit of *Cordia sebestena*, a gardening plant material was utilized in the form of CSAC prepared by chemical impregnation with H_3PO_4 (CSAC) and the saw dust of the fruit is coated with polypyrrole (polypyrrole composite) (called PPC) for the removal of Direct Green 6 (DG6) from aqueous solution. *C. 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. The fruit of this plant does not have any economical importance and usually it is not used for edible purpose. Furthermore, it has also been proved to be a good and low-cost precursor material for the development of CSAC. However, no literature has reported for the adsorption of dyes onto CSAC and PPC prepared from the fruit of *C. sebestena* (CS).

2. Materials and methods

2.1. Adsorbent preparation

2.1.1. Preparation of CSAC

The fruit of *C. sebestena* is collected from the local area. It is washed several times with water to remove particles and waste adhered on the surface followed by double-distilled water. It is then dried in sunlight for a week. The dried material is soaked in a boiling solution of 35% H_3PO_4 for one hour and then kept as such at room temperature for 1 d. After then, the material is separated, air dried and carbonized in muffle furnace at 550℃ for 1 h 30 min. The carbonized material then powdered and activated at 800℃ for 10 min. The resulting carbon was washed with plenty of water until the residual acid was removed. The dried material was ground well to fine powder and sieved into a particle size of 180–300 micron [22].

2.1.2. Preparation of PPC

The sawdust of the fruit of the gardening plant material *C. sebestena* was used for the preparation of polymer composite. The sawdust was first washed with distilled water in order to remove impurities and finally dried at 333 K for 2 h [23]. The polypyrrole was synthesized on sawdust surface, which was previously soaked in monomer pyrrole solution (0.2 M) for 12 h at room temperature followed by slow addition of chemical oxidants 0.5 M $FeCl_3$ at room temperature for 4 h [24]. The polymer-coated sawdust was designated as PPC and it was filtered, washed with distilled water and dried.

2.1.3. Adsorbate

The adsorbate DG6 [chemical formula = $C_{34}H_{22}N_8Na_2O_{10}S_2$, C.I. 30295, M.W: 812.69, λ_{max}: 593 nm, nature = direct dye which is anionic dye] was obtained from Erode Dye Company and its stock solution was prepared with double-distilled water. Experimental solutions of the required concentrations were obtained by successive dilutions with distilled water. The concentration of the dye was determined using Elico make BL-198 UV–visible spectrophotometer. The structure of DG6 is presented in Fig. 1.

2.1.4. Batch experiments

Batch adsorption experiments were conducted by shaking 0.1 g of CSAC and PPC with 100 ml of aqueous solution of dyes at different concentrations, time, temperatures and pH values. The pH values ranged from 2.0 to 11.0 were used by having HCl and NaOH solutions for pH adjustment. The adsorbent was removed by centrifugation and the concentration of dye in the supernatant liquid was determined spectrophotometrically (Elico make BL-198).

2.1.5. Characterization studies

Physicochemical characteristics of CSAC and PPC prepared from the fruit of *C. sebestena* plant material were studied as per the standard testing methods [25,26] and it is given in Table 1.

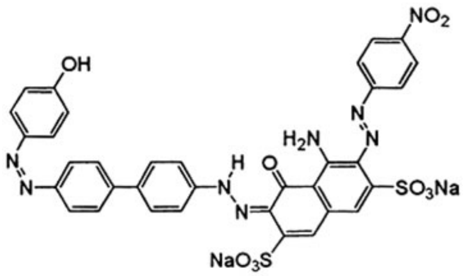

Fig. 1. Structure of DG6.

Table 1
Physicochemical characteristics of adsorbents

S. No.	Properties	CSAC	PPC
1	pH	7.2	7.81
2	Conductivity (mS cm^{-2})	0.586	6.599
3	Moisture content (%)	5.4	8.3
4	Ash (%)	17.82	16.67
5	Volatile matter (%)	18.90	57.63
6	Bulk density (g/mL)	0.53	0.29
7	Specific gravity	1.46	0.58
8	Porosity (%)	63.69	50.0
9	Methylene blue value (mg/g)	202	39
10	Iodine number (mg/g)	418.77	67

The CSAC which is prepared from phosphoric acid impregnation method possesses high conductivity value, high porosity, high surface area, methylene blue value and iodine number when compared to all other CSACs prepared from other chemical reagents. All these statements, strongly predicts that CSAC is chosen as best CSAC (adsorbent) than other CSAC.

2.1.6. *Desorption studies*

In order to find out the possibility of desorption for frequent applications, the regeneration of the used adsorbent was also investigated. Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. For performing this study, the supernatant was separated after centrifugation and the adsorbents (CSAC and PPC) were separated and allowed to agitate with 50 ml of distilled water at different pH (2–11) above the equilibrium time of adsorption. The desorbed dye solution was separated by centrifugation and estimated as given in the adsorption studies [27].

3. Results and discussion

3.1. *Effect of agitation time and initial dye concentration*

Fig. 2(a) and (b) represents the effect of initial dye concentration and contact time for the removal of DG6 by CSAC and PPC. For this study, 100 ml of 25–100 mg/L of dye solution agitated with 100 mg of adsorbent. The amount of DG6 removed by CSAC increases from 16.10 to 53.12 mg/g and by PPC, it increases from 20.66 to 75.86 mg/g while increasing the initial concentration from 25 to 100 mg/L. Rapid uptake of dye noticed at the initial 80 min of contact time for both the adsorbents CSAC and PPC. The initial rapid uptake is due to the concentration gradient created by the vacant adsorbent surface between adsorbate in solution and adsorbate on the carbon [28]. Availability of dye molecules near adsorbent also increased while increasing the concentration which results in high uptake of dye at higher concentration [28].

Based on this result, the adsorption of DG6 by CSAC and PPC reaches the equilibrium around 100 min for all the ranges of concentrations studied beyond which there is no change in the adsorption capacity and therefore 100 min is fixed as equilibrium time for isotherm studies for both the adsorbents. The maximum percentage of dye removal at equilibrium time was 64.41% for CSAC and 82.65% for PPC at 25 mg/L of initial dye concentration.

Similar behaviours were reported for the adsorptive removal of Direct Blue 67 by low-cost rice husk waste [29] and Direct Blue 71 by TPAC and PPC prepared from Thevetia Peruviana [30].

The amount of DG6 removal by CSAC is less than that of PPC. From the literature [31], 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.

3.2. *Effect of pH*

Fig. 3(a) and (b) represents the effect of pH on DG6 dye adsorption. The percentage of dye adsorption by CSAC was maximum at pH 2 and for PPC was maximum at pH 4 and decreased on increasing the pH. Thus, the results showed that the uptakes were much higher in acidic solution than those in neutral and alkaline conditions. This is due to the increasing electropositive charge of the adsorbent which favoured the adsorption of dye anions due to the electrostatic attraction [32].

Similar result was reported for the adsorptive removal of Direct Blue 71 by TPAC and PPC prepared from Thevetia Peruviana [30].

3.3. *Effect of temperature*

The effect of temperature on the adsorption process of DG6 onto CSAC and PPC was investigated at three temperatures: 30, 40 and 50˚C. As it is presented in Fig. 4(a) and (b) and Table 2, the sorption efficiency increases by raising the temperature for both the adsorbents CSAC and PPC. At high temperature, the diffusion rate of the dye molecules and their kinetic energy increases through the external boundary layer and internal sites of the sorbent [33,34].

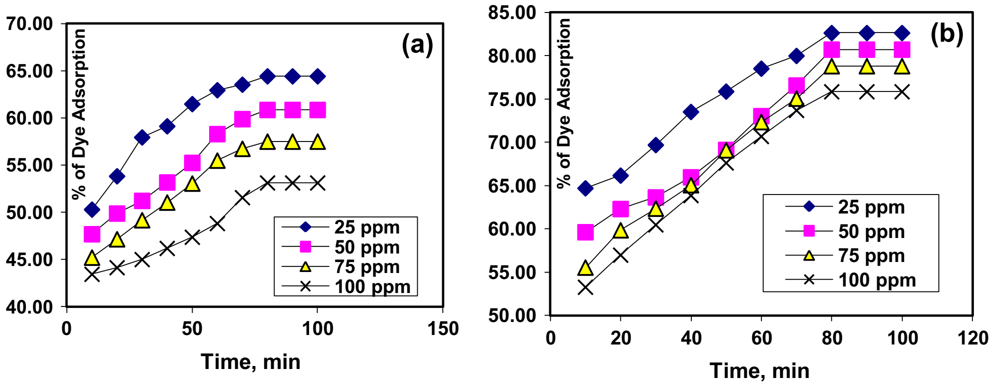

Fig. 2. (a) Effect of agitation time on the percentage removal of DG6 dye on CSAC at 30˚C and (b) effect of agitation time on the percentage removal of DG6 dye on PPC at 30˚C.

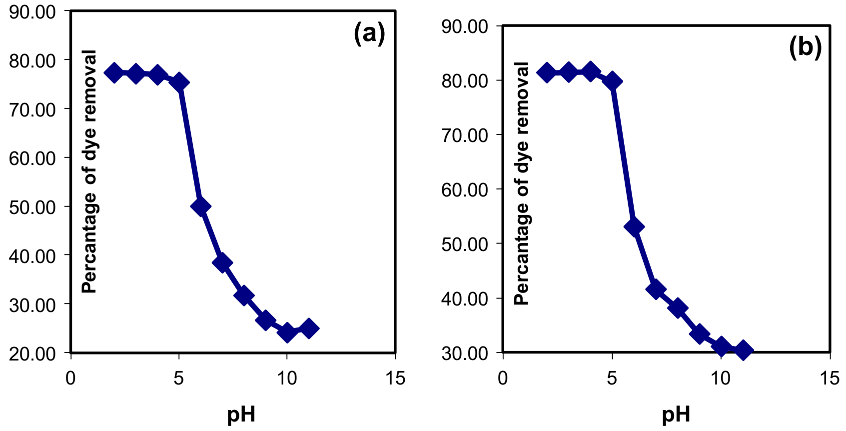

Fig. 3. (a) Effect of pH on CSAC and (b) effect of pH on PPC.

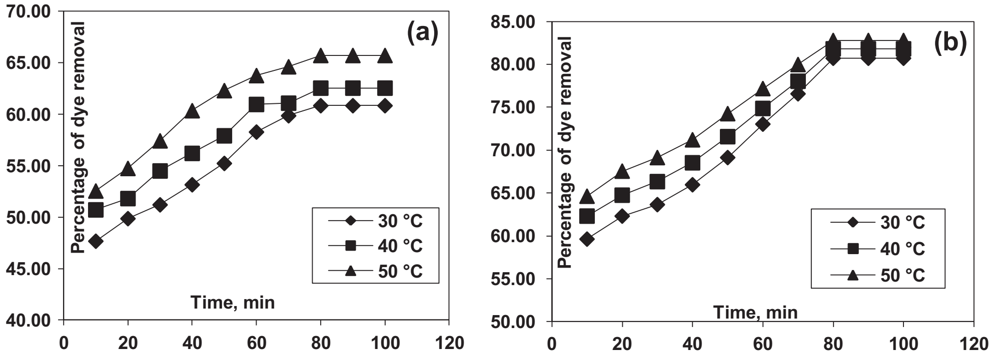

Fig. 4. (a) Effect of temperature on the adsorption of DG6 dye onto CSAC at initial concentration of 50 mg/L and (b) effect of temperature on the adsorption of DG6 dye onto PPC at initial concentration of 50 mg/L.

Table 2
Calculated kinetic parameters for the adsorption of DG6 onto CSAC and PPC at various initial dye concentrations and at various temperatures

	CSAC						
	Initial dye concentration (mg/L)				Temperature (℃)		
Parameter	25	50	75	100	30	40	50
$q_{\mathrm{e\ exp}}$ (mg/g)	16.10	30.43	43.13	53.12	30.43	31.28	32.87
Pseudo-first-order kinetics							
$k_1 \times 10^{-2}$ (min^{-1})	4.65	4.03	4.37	2.60	4.03	3.80	4.21
$q_{\mathrm{e\ cal}}$ (mg/g)	6.620	13.708	13.492	16.076	13.7088	11.2538	12.5400
r^2	0.9779	0.8638	0.8917	0.7883	0.8638	0.9115	0.9725
Pseudo-second-order kinetics							
$k_2 \times 10^{-4}$ (g/mg min)	126.6	47.7	36.8	27.8	47.7	57.4	58.5
h	3.6127	5.0000	7.6687	8.7719	5.0000	6.2150	7.0028
$q_{\mathrm{e\ cal}}$ (mg/g)	16.89	32.36	45.66	56.18	32.36	32.89	34.60
r^2	0.9995	0.9972	0.9981	0.9952	0.9972	0.9984	0.9992
	PPC						
$q_{\mathrm{e\ exp}}$ (mg/g)	20.66	40.37	59.11	75.86	40.37	40.91	41.40
Pseudo-first-order kinetics							
$k_1 \times 10^{-2}$ (min^{-1})	3.270	2.510	2.902	3.662	2.510	2.556	2.879
$q_{\mathrm{e\ cal}}$(mg/g)	7.6225	16.3681	27.1706	41.3713	16.3680	15.1216	14.6926
r^2	0.9644	0.88	0.9421	0.9178	0.88	0.8951	0.8996
Pseudo-second-order kinetics							
$k_2 \times 10^{-4}$ (g/mg min)	71.0	23.7	16.0	13.0	23.7	27.2	32.5
h	3.4153	4.5579	6.6534	8.8810	4.5579	5.2770	6.3052
$q_{\mathrm{e\ cal}}$ (mg/g)	21.93	43.86	64.52	82.64	43.86	44.05	44.05
r^2	0.9979	0.9911	0.9941	0.9959	0.9911	0.9936	0.996

The percentage of DG6 sorption by CSAC increases from 60.85 to 65.73% and by PPC increases from 80.73 to 82.80% while increasing the temperature from 30 to 50℃. Thus, the results indicate that the sorption of DG6 by CSAC and PPC is endothermic in nature. Similar behaviour was observed for the adsorptive removal of DB 53 by EAAC [28].

Increasing temperature may produce a swelling effect within the internal structure of the adsorbents enabling large dyes to penetrate further. Thus, the adsorption process becomes more favourable with increasing temperature. At certain temperature (here above 50℃), swelling effect may not takes place as it attains saturation. Hence no change is observed after 50℃.

3.4. Adsorption kinetics

Two simplified kinetic models were followed to determine the mechanism of the adsorption process; Lagergren pseudo-first-order and pseudo-second-order models.

The Lagergren pseudo-first-order equation is given as:

$$\log(q_{\mathrm{e}} - q_{\mathrm{t}}) = \log q_{\mathrm{e}} - \left(\frac{K_1}{2.303}\right)t \tag{1}$$

where q_{e} and q_t = the amount of DG6 adsorbed (mg/g) at equilibrium and at time t (min), respectively. K_1 = the first-order rate constant (mm^{-1}).

Values of K_1 at (30℃) were calculated for both CSAC and PPC from the plots of $\log(q_{\mathrm{e}} - q_t)$ vs. t (figure not shown) for different initial concentrations of DG6 and for different temperatures. The r^2 values obtained were poor and the experimental q_{e} values did not agree with the calculated values obtained from the linear plots (Table 2). It showed that Lagergren pseudo-first-order model does not applicable.

The pseudo-second-order equation is expressed as:

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

where K_2 (g/mg min) is the rate constant of second-order adsorption.

Values of K_2 were calculated for both CSAC and PPC from the plot of t/q_t vs. t as shown in Figs. 5(a) and (b) and 6(a) and (b). The values of r^2 are greater than 0.99 for all DG6 concentrations for both CSAC and PPC. It showed a good agreement between the experimental and the calculated q_e values (Table 2) indicating the applicability of this model.

In case of PPC, the adsorption capacity is due to its ion exchangeable active sites. Polypyrrole 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 polymer [24]. Therefore, higher percentage removal of anionic dyes by the polymer composite is supposed to occur by ion-exchange mechanism due to exchangeable active sites and explained by pseudo-second-order kinetics.

3.5. Adsorption isotherms

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes [35]. The adsorption isotherm study was carried out on two isotherm models; Langmuir [36] and Freundlich [37]. The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients r^2 values.

3.6. Langmuir isotherm

The Langmuir isotherm tells towards surface homogeneity. The monomer coverage of the sorbate on a sorbent surface at constant temperature is represented by the Langmuir isotherm.

The linearized form of the equation can be represented as:

$$\frac{1}{q_e} = \frac{1}{kC_e q_m} + \frac{1}{q_m} \tag{3}$$

where C_e is the concentration of the sorbate at equilibrium, q_e is the amount of sorbate sorbed at equilibrium per unit mass of sorbent, q_m is the monolayer capacity, k is the adsorption equilibrium constant.

A plot of C_e/q_e vs. C_e was drawn which gives a straight line. The slope and the intercept of this line give the value of q_m and k. The adsorption capacity of the CSAC for DG6 as obtained from the Langmuir plot is 112.35 mg/g and for PPC is 212.76 mg/g at 30°C. The adsorption equilibrium constant, k, value obtained for CSAC is 0.0185 dm^3/mg and for PPC is 0.0220 dm^3/mg at 30°C.

It can be noticed that the value of q_m decreases with an increase in the temperature when the temperature is above 30°C till the temperature reaches 50°C. This is because the increase in temperature leads to an increase in the speed of adsorption process and also the adsorption process is considered to be a physical adsorption. In addition, because the adhesion of dye molecules is weak in such desorption process starts once the temperature is increased. This causes a decrease in the value of q_m at high temperature.

3.7. Freundlich isotherm

The Freundlich adsorption isotherm indicates the surface heterogeneity of the sorbent. The linearized form of this isotherm is expressed as:

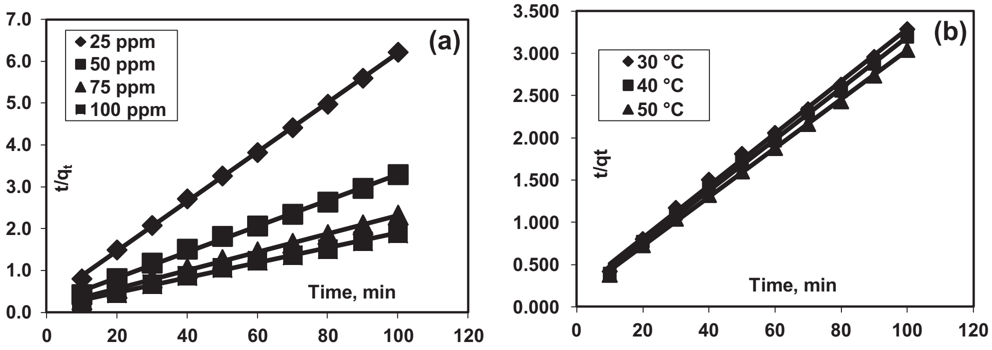

Fig. 5. (a) Pseudo-second-order plots for the adsorption of DG6 dye onto CSAC at different initial dye concentrations and (b) pseudo-second-order plots for the adsorption of DG6 dye onto CSAC at different temperatures.

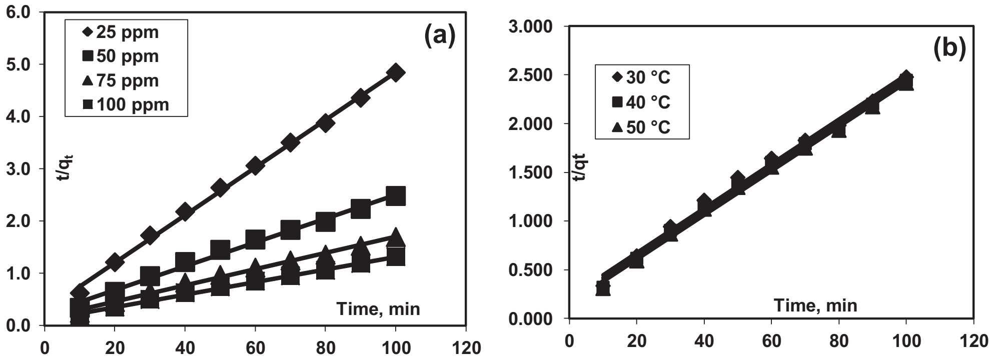

Fig. 6. (a) Pseudo-second-order plots for the adsorption of DG6 dye onto PPC at different initial dye concentrations and (b) pseudo-second-order plots for the adsorption of DG6 dye onto PPC at different temperatures.

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{4}$$

where K_f and n are the Freundlich coefficients, obtained from the plots of log q_e vs. log C_e.

When the Freundlich isotherm model was applied to analyse the adsorption process for both CSAC and PPC (Fig. 7(a) and (b)), the adsorption coefficients calculated (Table 3) are K_f = 2.8099 mg/g and n = 1.29 for CSAC and K_f = 5.1951 mg/g and n = 1.17 for PPC at 30˚C. The Freundlich constant K_f increases with an increase in the temperature and the value of n is greater than 1.0 indicating the adsorption process is favourable.

When the correlation coefficients (r^2) values of two models were compared (Table 3), it was noted that the r^2 value of the Freundlich plot was higher than that of the Langmuir plot. It shows, it is well fitted with Freundlich model. It suggests the formation of multilayer adsorption and also the surface is energetically heterogeneous.

The maximum adsorption value, q_m (mg/g) obtained in the present study was compared with those of other sorbents for direct dye category adsorption (Table 4). Our research group have reported the q_m value [30,38] for the CSAC prepared from *Euphorbia tirucalli* wood, CSAC prepared from Thevetia Peruviana wood and polypyrrole polymer composite prepared from Thevetia Peruviana wood sawdust is high when compared with our present study. At the same time, q_m value obtained from other two adsorbents presented in Table 4 is low when compared with our adsorbent. Hence, the results of this comparison showed that CSAC and PPC has great potential as a sorbent for DG6 adsorption and can compete favourably with other sorbents that have been studied.

3.8. Thermodynamic study

The data obtained at different temperatures can be used to evaluate the thermodynamic parameters like Gibbs free energy ($\Delta G°$), enthalpy charges ($\Delta H°$) and entropy changes ($\Delta S°$).

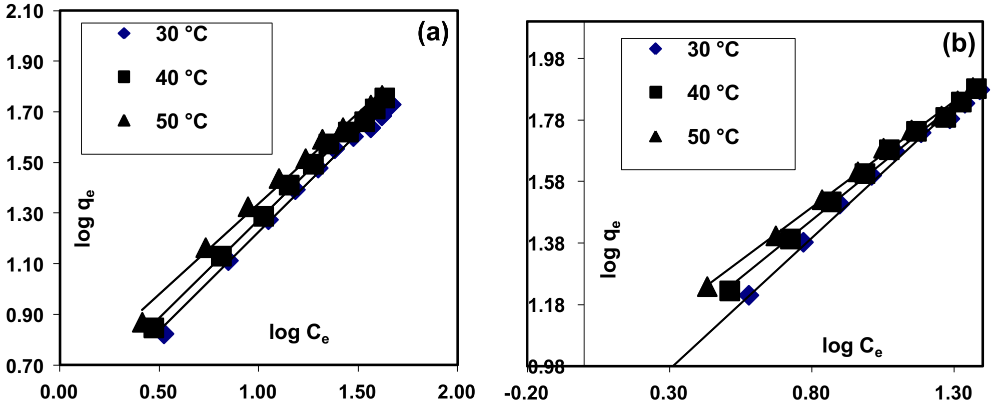

Fig. 7. Freundlich plot for the adsorption of DG6 dye onto CSAC and (b) Freundlich plot for the adsorption of DG6 dye onto PPC.

Table 3.
Results of isotherm plots for the adsorption of DG6 onto CSAC and PPC

	CSAC			PPC		
	Temperature (°C)			Temperature (°C)		
Parameter	30	40	50	30	40	50
Freundlich isotherm						
n	1.29	1.29	1.40	1.17	1.33	1.45
k_f ($\text{mg}^{1-1/n}\ \text{L}^{1/n}\ \text{g}^{-1}$)	2.8099	3.1586	4.1773	5.1951	7.1630	8.8023
r^2	0.9938	0.9968	0.9909	0.9937	0.9956	0.9977
Langmuir isotherm						
q_m (mg/g)	112.3596	120.4819	100	212.766	161.2903	129.8701
b_L (L/mg)	0.018526	0.019311	0.03012	0.02206	0.03543	0.05457
r^2	0.9805	0.9631	0.9788	0.9618	0.9778	0.9541

Table 4
Comparison of the Langmuir sorption capacity (q_m in mg/g) of different sorbents for different direct dyes

Adsorbent	Adsorbate	Q_o in mg/g	Refs.
Present study Activated carbon from *Cordia Sebestena* fruit(CSAC4)	Direct green 6	112.35 (30°C) 120.48 (40°C)	–
Polypyrrole polymer composite obtained from fruit sawdust from *Cordia Sebestena* (PPy/SD)	Direct green 6	100.00 (50°C) 212.76 (30°C) 161.29 (40°C) 129.81 (50°C)	
Activated carbon from *Euphorbia tirucalli* wood	Direct Blue	192.30	[38]
Activated carbon from Thevetia Peruviana wood	Direct blue 71	196.08	[30]
Polypyrrole polymer composite prepared from Thevetia Peruviana wood sawdust	Direct Blue 71	344.83	[30]
Modified magnetic ferrite nanoparticle	Direct Green 6	64.10	[39]
	Direct Red 31	55.55	
	Direct Red 23	26.11	

They are:

$$\Delta G^\circ = -RT \ln K_L \tag{5}$$

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H^\circ}{RT} \tag{6}$$

$$\Delta S^\circ = \Delta H^\circ - \frac{\Delta G^\circ}{T}. \tag{7}$$

A plot of $\ln K_L$ vs. $1/T$ gives a straight line. The slope and intercept of the plot give the values of ΔH° and ΔS°, while ΔG° were calculated using the above equation. The values associated with the thermodynamic parameters are listed in Table 5.

Table 5
Thermodynamic parameters for the adsorption of DG6 onto CSAC and PPC

Temperature (°C)	CSAC			PPC		
	ΔH° kJ/mol	ΔS° kJ/K/mol	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° kJ/K/mol	ΔG° kJ/mol
30	14.96	0.05526	−1.7807	16.76	0.0681	−3.8743
40			−2.3333			−4.5553
50			−2.8859			−5.2363

Negative values of ΔG° for both CSAC and PPC in all temperatures indicate the feasibility of the process and spontaneous nature of the adsorption. Positive values of ΔH° for both CSAC and PPC indicate the endothermic nature of the adsorption. The values of ΔS° were positive indicating favourable randomness.

Gibb's free energy ΔG° representing the driving force for the affinity of the dye molecules for the adsorbents CSAC and PPC because of its negative values at all temperatures.

3.9. Desorption study

Maximum desorption of DG6 is 28.3% for CSAC and 39.6% for PPC at a pH range of 6–8. On increasing the pH above 8, there is no change in desorption of DG6.

4. Conclusion

The use of the fruit of the gardening plant material *C. sebestena* as adsorbent in the form of CSAC and PPC for the removal of DG6 from aqueous solutions was investigated. A comparative study was also made between the two adsorbents (CSAC and PPC). The percentage removal of DG6 by 0.1 g of CSAC at a temperature of 30°C with initial dye concentration of 50 ppm having 3 h time duration was found to be 60.85% and for PPC with same condition was found to be 80.73%.The adsorption of the dye increased with an increase in the temperature from 30 to 50°C indicates that the adsorption is endothermic in nature for both the adsorbents, which was well supported by positive ΔH° values. Kinetic studies showed that adsorption of DG6 followed pseudo-second-order model for both the adsorbents. Freundlich model is more appropriate for both the adsorbents to explain the nature of adsorption with high correlation coefficient rather than Langmuir model. The maximum monolayer adsorption capacity calculated by Langmuir model for DG6 at 30°C was 112.35 mg/g by CSAC and 212.76 mg/g by PPC. Thermodynamic analysis showed that the removal of DG6 is endothermic, favourable and spontaneous in nature. The maximum per cent of desorption observed at pH 6–8 was 28.3% for CSAC and 39.6% for PPC. Thus, the currently introduced adsorbents are both simple and good for the adsorption process. But based on the results obtained in this study, it can be concluded that PPC is an effective, superior and alternative adsorbent for the removal of DG6 from aqueous solutions when compared with CSAC.

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