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Equilibrium and kinetic studies for the adsorption of Basic Red 29 from aqueous solutions using activated carbon and conducting polymer composite

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ABSTRACT

The paper deals with the study on application of activated carbon (*Cordia sebestena* activated carbon (CSAC)) and polypyrrole polymer composite prepared from the precursor fruit of the gardening plant material *Cordia sebestena* for the removal of cationic dye (basic dye namely Basic Red 29 (BR29)) from aqueous solutions. 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 wastes like sawdust coated with polypyrrole called polypyrrole polymer composite is an efficient adsorbent for the removal of cationic dye BR29 from aqueous solutions when compared to activated carbon (CSAC).

Keywords: Polypyrrole; *Cordia sebestena*; Adsorption; Basic Red 29; Equilibrium and kinetic studies

1. Introduction

Colour is the most obvious indicator of water pollution. Wastewater containing dyes discharged from various industries, in particular, textile industry often causes many environmental problems [1,2]. Maximum dyes are highly soluble in water and so their removal from wastewater is highly difficult [3]. Even dyes at very low concentrations in the effluent are highly visible and are considered undesirable. The coloured wastewater is considered toxic for aquatic biosphere and affected symbiotic process by reducing the photosynthetic activity [4,5]. Several methods such as coagulation/flocculation [6], chemical oxidation [7], membrane separation [8], adsorption [9], electrochemical reduction [10], and microbiological decomposition [11] have been developed to remove colour from dye-containing effluent which vary in effectiveness, economic cost and environmental impact. Currently, the sorption technique is proven to be an effective and attractive process for the treatment of the coloured wastewater. Due to their diversity in surface and porosity, high physical-chemistry stability, regeneration and reuse for continuous process, polymeric adsorbents such as polyaniline, polypyrrole, polystyrene, polymaleic anhydride, polymethyl methacrylate and their derivatives have been used as alternatives to activated carbon in removal and recovery of organic pollutants from industrial wastewater [12,13].

In this study, the adsorption of basic dye namely Basic Red 29 (BR29) has been investigated using *Cordia sebestena* activated carbon (CSAC) and polypyrrole

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polymer composite (PPC) as adsorbents. The adsorbents are prepared from the precursor fruit of the gardening plant material called *Cordia sebestena* (*C. Sebestena*). 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 activated carbon and polymer composite. The kinetic and thermodynamic parameters are calculated to determine the adsorption mechanism. The effects of initial dye concentration, agitation time, pH and temperature has been evaluated to assess the possibility of CSAC and PPC for the removal of BR29.

2. Materials and methods

2.1. Preparation of activated carbon (CSAC)

Activated carbon is prepared from the precursor, fruit of the gardening plant material *C. sebestena*. The fruit is dried in sunlight for 10 d. The dried material is soaked in a boiling solution of 35% H_3PO_4 for 1 h and kept at room temperature for 24 h. The material is separated, air-dried and carbonized in muffle furnace at 550°C for 1½ h. This carbonized material is powdered and activated at 800°C for 10 min. The resulting carbon is washed with plenty of water until the residual acid is removed. The dried material is ground well to fine powder and sieved into a particle size of 180 to 300 micron [14].

2.2. Preparation of PPC

PPC is synthesized on the sawdust surface of the fruit of *C. sebestena*. In order to prepare polymer composite, 5.0 g sawdust immersed in 50 ml of 0.2 M freshly distilled pyrrole before polymerization. The excess monomer solution is removed by simple decantation. Then, 50 ml of 0.5 M ferric chloride as an oxidant solution is added into the mixture gradually, and the reaction is allowed to continue for 4 h at room temperature. The PPC is filtered, washed with distilled water, dried in an oven at about 60°C and sieved before use [15]. The coating percentage of each polymer onto sawdust is determined by weight difference of the dried sawdust before and after coating and it is nearly 5% [16].

2.3. Preparation of BR29 dye solution

The basic dye used in the current study is BR29, and it has the molecular formula: $C_{19}H_{17}ClN_4S$, M.Wt: 368.98 g/mol with CI number 11,460 and λmax: 511 nm. The dye is used in the same condition as received from dyeing unit, Erode, without further purification. The structure of BR29 is presented in Fig. 1. A stock solution of dye (1,000 mg/L) is prepared by dissolving appropriate amount of dye (based on the percentage of purity) and suitably diluted as and when required. The concentration of the dye is determined using Elico make UV–vis spectrophotometer (BL 198). All the chemicals used were analytical reagent grades and used without further purification.

2.4. Batch mode adsorption experiments

Physico-chemical characteristics of the activated carbon and polymer composite prepared from the fruit of *C. sebestena* are studied as per the standard testing methods [17,18] and are given in Table 1. Adsorption experiments of BR29 onto CSAC and PPC are conducted by agitating 100 ml adsorbate solution of known concentration with 0.1 g of adsorbent. The mixture is agitated in a temperature-controlled shaker, and samples are withdrawn at different time intervals, centrifuged and analysed for remaining dye concentration. Equilibrium studies are conducted by agitating 100 ml of dye solution with 0.1 g of adsorbent at different initial dye concentrations and also at different temperatures.

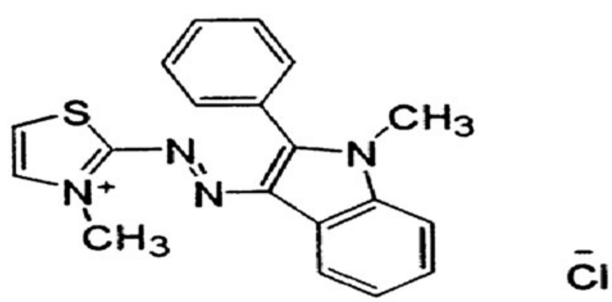

Fig. 1. Molecular structure of BR29.

Table 1
Physico-chemical characteristics of CSAC and PPC

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	Methylene blue value (mg g^{-1})	202	39
5	Iodine number (mg g^{-1})	418.77	67

2.5. Characterization studies

2.5.1. Scanning electron microscope (SEM)

Fig. 2(a) indicates the SEM micrograph of CSAC showing the rough areas on the surface of the carbon, and Fig. 2(b) indicates the SEM micrograph of PPC showing the formation of the polymer matrix on the surface of the sawdust.

2.5.2. Fourier transform infrared (FTIR)

Infrared spectra of Activated Carbon (CSAC), sawdust of the fruit material (SD) and PPC were measured with a Fourier transform infrared spectrophotometer to elucidate the functional group presenting in CSAC, SD and PPC, and the results were given in Table 2.

When comparing FTIR spectra of CSAC, SD and PPC, some of the peaks in SD have disappeared when sawdust is coated with the polymer polypyrrole. This confirms the formation of PPC over SD. The peak of 2,923.56 cm^{-1} in SD which corresponds to C–H stretching is not found in PPC. Similarly, the peak of 1,419.35 cm^{-1} that corresponds to C–O stretching and the peak of 619.038 cm^{-1} corresponds that to out of plane C–H bending mode are not found in PPC. This indicates that the polymer pyrrole has been coated over the sawdust of *C. sebestena*. The percentage of dye removal is high in PPC, and this is due to the surface modification of the sawdust by the polymer polypyrrole. Hence, the presence of these functional groups may be attributed for the enhancement of the percentage of dye removal in PPC. Similarly, there are no peaks found in SD and PPC in the region of 532.257 and 404.978 cm^{-1} which correspond to in-plane aromatic ring deformation vibration in Activated Carbon (CSAC). This confirms the formation of CSAC (Fig. 3).

3. Results and discussion

3.1. Effect of agitation time and initial dye concentration

The effect of initial concentration of dye on the percentage of the removal of BR29 on CSAC and PPC has been studied. On increasing the initial concentration of

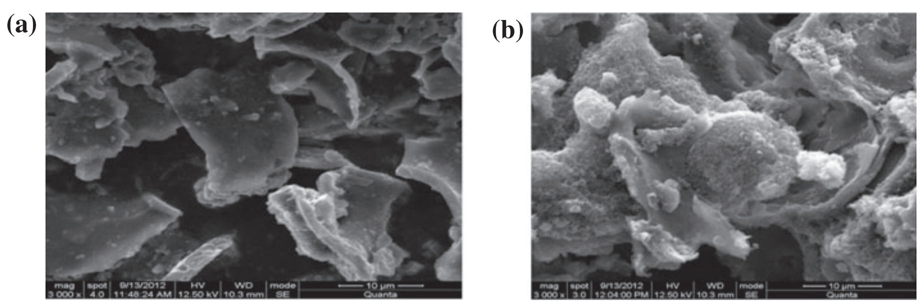

Fig. 2. (a) SEM image of CSAC; (b) SEM image of PPC.

Table 2
Peak assignments of functional groups of CSAC, SD and PPC

Peak positions/Samples				
CSAC	SD	PPC	Possible assignments	References
3,422.06	3,344.93	3,370	O–H stretching	[20]
2,922.59	2,923.56	–	C–H stretching	[21,24]
–	1,726.94	1,549.52	C=O str of carbonyl group	[22,23]
–	1,625.7	–		
–	1,419.35	–	C–O str and OH bending of alcohol and carboxylic acids	[19,23]
–	1,319.07	1,309.43		
–	1,265.07	1,168.65		
1,045.23	1,033.66	1,041.37		
–	–	900.694	–CH def	–
–	619.038	–	C–C stretching	[25]
532.257	–	–	Out of plane C–H bending mode	[26]
404.978	–	–	In-plane aromatic ring deformation vibration	[27]

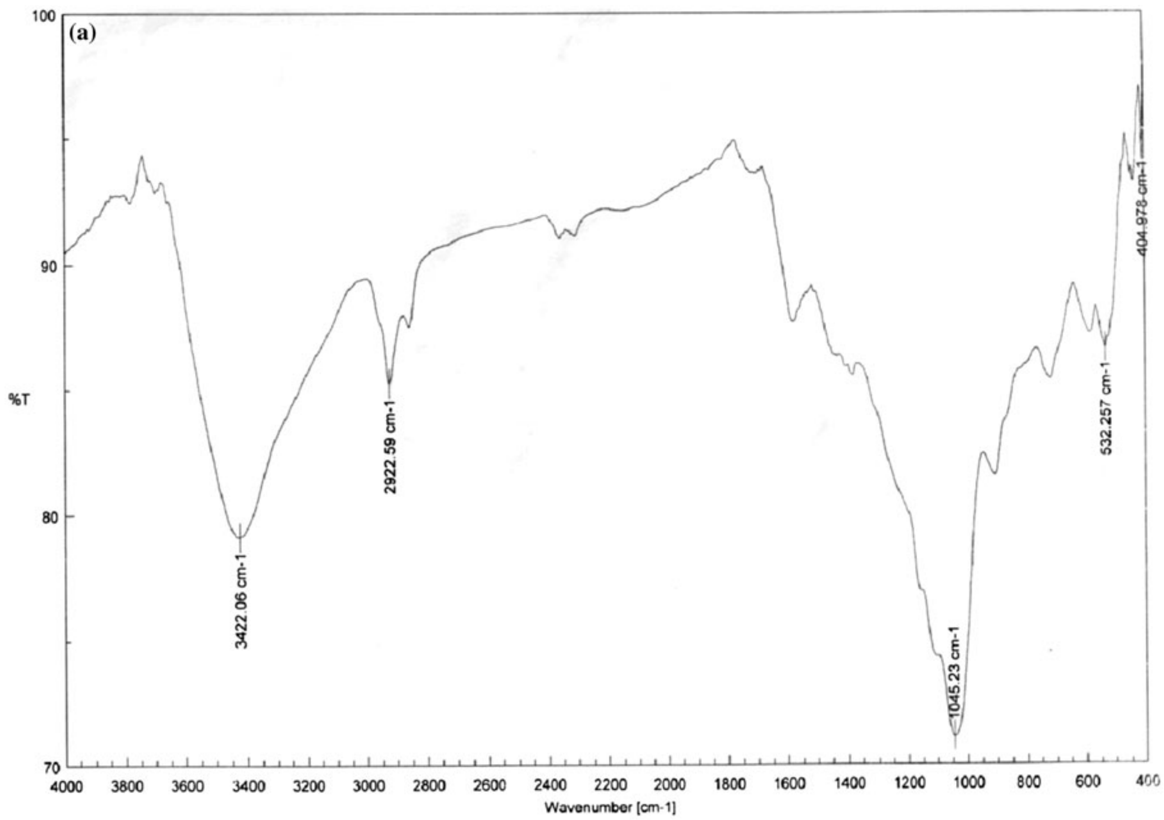

Fig. 3(a). FTIR spectra of CSAC.

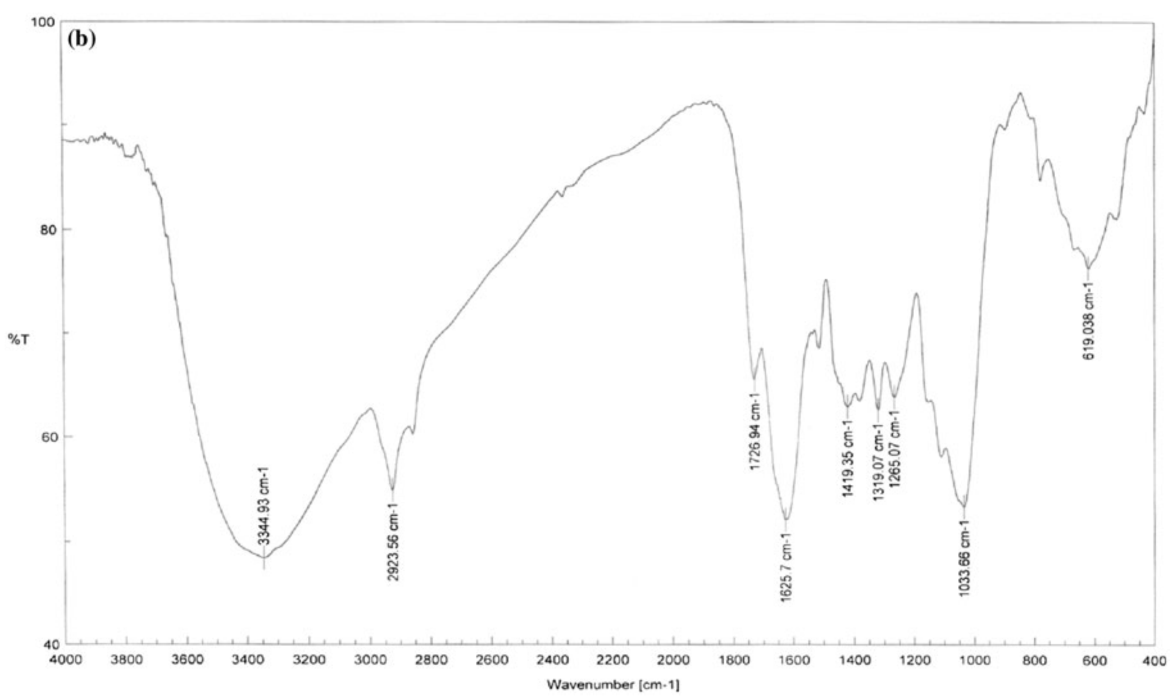

Fig. 3(b). FTIR spectra of SD.

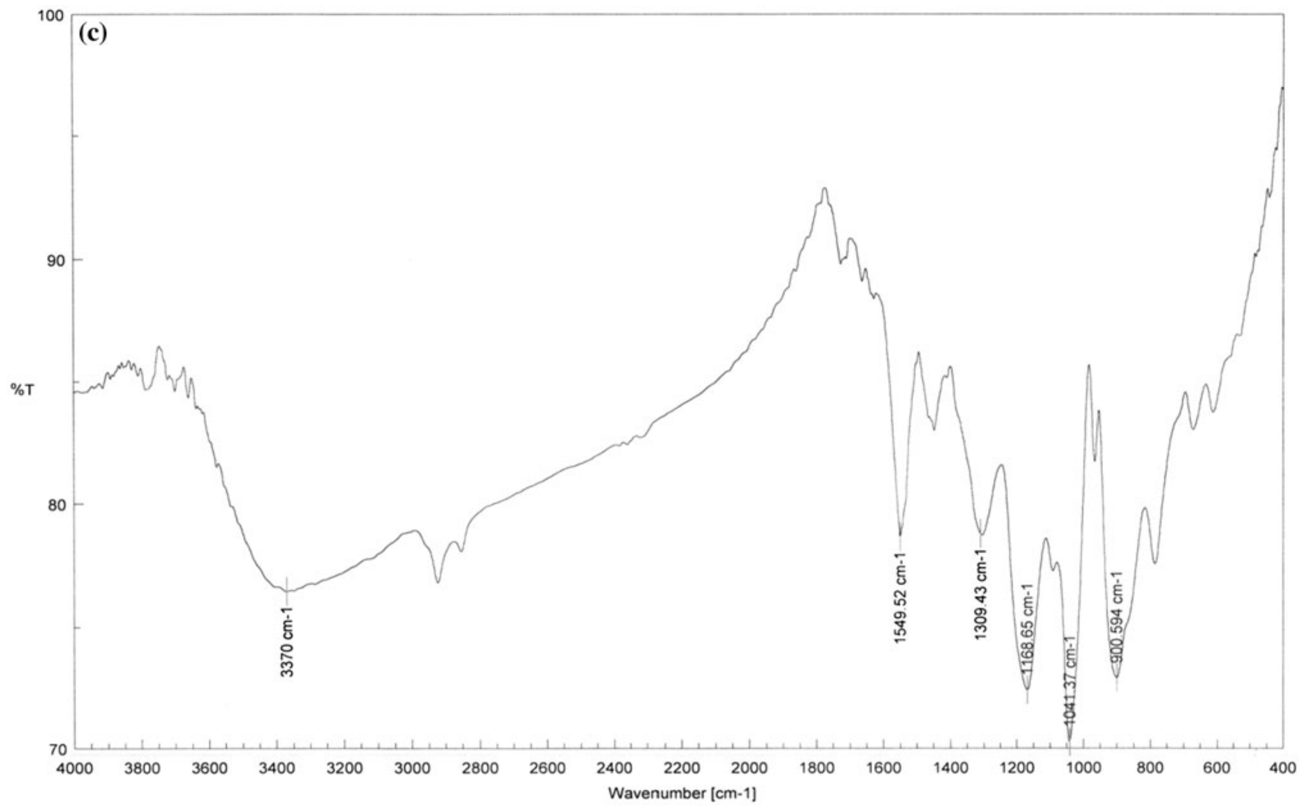

Fig. 3(c). FTIR spectra of PPC.

the dye, the percentage of the removal of dye is decreased although the amount of dye adsorbed per unit mass of adsorbent is increased. The percentage of dye removal is decreased from 71.40 to 63.56% for CSAC and from 87.10 to 79.96% for PPC while increasing the initial dye concentrations from 25 to 100 mg/L. These decreases in percentage of removal are due to the lack of available active sites for adsorption. The variation in the percentage of the removal of BR 29 with contact time at an initial dye concentration of 50 mg/L by various adsorbents such as CSAC and PPC is shown in Fig. 4.

It is observed that the maximum amount of dye is adsorbed within the contact time of 80 min and after that, there is no change for both the adsorbents. The adsorption capacity at equilibrium is increased from 17.85 to 63.56% mg/g for CSAC and from 21.78 to 79.96% mg/g for PPC 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 the adsorbent. Similar trend has been reported for the adsorption of methylene blue by polyaniline coated on wood sawdust [28], malachite green using activated carbon prepared from Euphorbia Tirucalli wood [29], methylene blue by polyaniline conducting polymer

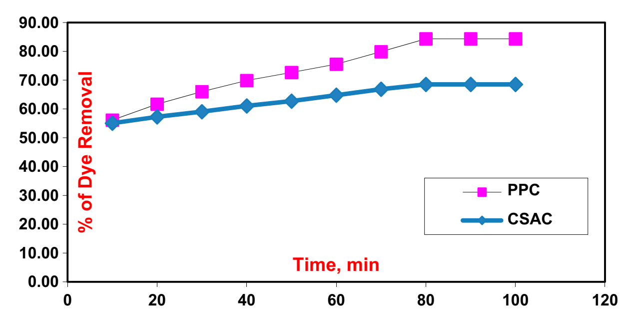

Fig. 4. Effect of agitation time on the percentage removal of BR 29 dye on CSAC and PPC at 30˚C (Initial dye concentration of 50 mg/L).

[30], Basic Violet 3 and Basic Violet 10 by biomaterial Euphorbia Tirucalli wood [31].

3.2. 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 BR29 onto CSAC and PPC has been investigated and shown in Figs. 5(a) and (b). The

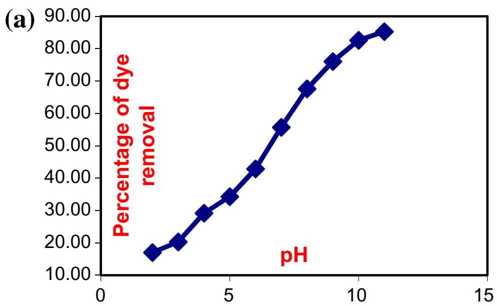

Fig. 5(a). Effect of pH for adsorption of BR29 onto CSAC.

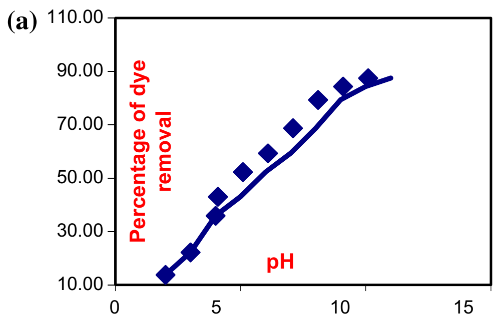

Fig. 5(b). Effect of pH for adsorption of BR29 onto PPC.

maximum percentage removal of 85.29% for CSAC and 87.50% for PPC occurs at a high pH of 11 for both the adsorbents. It is noted that when pH increases, the extent of dye removal also increases. Moreover, the electrostatic repulsion between the positively charged BR 29 and the surface of adsorbent is lowered, and consequently, the removal efficiency is increased. Similar trend has been reported for the adsorption of methylene blue by polyaniline coated on wood sawdust [28].

3.3. Effect of temperature

The effect of temperature on dye adsorption has been studied at 30, 40 and 50˚C and shown in Figs. 6(a) and (b). The results indicate that the amount of dye adsorbed at equilibrium increases with the increasing temperature. This may be a result of the increase in the mobility of the dye molecules with an increase in temperature [32]. The equilibrium adsorption increases from 68.53 to 75.27% for CSAC and from 84.33 to 89.20% for PPC indicating that the adsorption is an endothermic process. Similar trend is noticed for the adsorption of reactive red 195 by polypyrrole composite prepared from Euphorbia Tirucalli L wood [33].

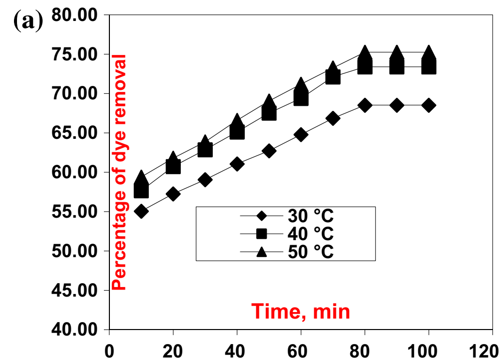

Fig. 6(a). Effect of temperature on the percentage removal of BR 29 dye on CSAC.

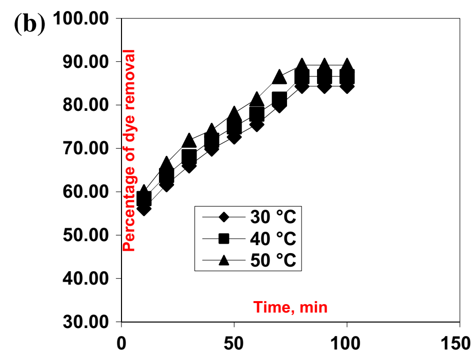

Fig. 6(b). Effect of temperature on the percentage removal of BR 29 dye on PPC.

3.4. Kinetic studies

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for validating the efficiency of the process. In the present work, the kinetic data obtained from batch studies have been analysed using pseudo-first-order, second-order and intra-particle diffusion models.

3.5. Pseudo-first-order kinetics

Lagergren [34] has suggested a first-order equation for the sorption of liquid/solid system based on solid adsorption capacity. The Lagergren rate equation is the most widely used adsorption rate equation for the adsorption of adsorbate from aqueous solution. The first-order equation is

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (1)$$

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 ($q_e - q_t$) vs. t should give a straight line with a slope of—k_1/2.303 and intercept log q_e.

The calculated values of k_1 and q_e are summarized for the adsorption of BR29 on CSAC and PPC (figure not shown) at different initial dye concentrations and at different temperatures are given in Tables 3a and 3b. It is found that an irregular trend was noticed while increasing the dye concentration and temperature, which may be due to poor fit of the data with the pseudo-first-order kinetic model. Furthermore, large deviation is noticed between the experimental q_e (exp) and calculated q_e (cal) values, and also, the r^2 values suggest that the adsorption data fit poor to pseudo-first-order kinetics. Hence, adsorption of BR29 onto CSAC and PPC does not obey the Lagergren pseudo-first-order kinetic model.

3.6. Pseudo-second-order kinetics

The adsorption may also be described by pseudo-second-order kinetics [35] if the adsorption does not follow the first-order kinetics. The pseudo-second-order kinetic equation is expressed as

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

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

The initial adsorption rate, h, (mg/g/min) is expressed as $h = k_2 q_e{}^2$. The values of k_2 and q_e are determined from the intercept and slope of the plot.

The pseudo-second-order plot for the adsorption of BR29 on CSAC and PPC shown in Figs. 7(a) and (b) at various initial dye concentrations and temperatures are given in Tables 3a and 3b. It is found that the pseudo-second-order rate constant, k_2, decreases with an increase in dye concentration (94.4×10^{-4} g/mg min to 21.2×10^{-4} g/mg min) for CSAC and also for PPC (4.2×10^{-4} g/mg min to 4.4×10^{-4} g/mg min) from 25 to 100 mg/L. Furthermore, q_e (cal) and q_e (exp) are well in close at various dye concentrations as well as at various temperatures of study. It is found that the correlation coefficient r^2 is higher than pseudo-first-order model. Similar trend was noticed for the adsorption of basic violet 10 by biomaterial Euphorbia Tirucalli wood [31]. From the result, it can be suggested that the pseudo-second-order describes the adsorption of BR29 by CSAC and PPC much better than pseudo-first-order model.

3.7. Intraparticle diffusion model

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent. Weber and Morris [36] have suggested the following kinetic

Table 3a
Calculated kinetic parameters for the adsorption of BR29 onto CSAC at various initial dye concentrations and at various temperatures

	CSAC						
	Initial dye concentration (mg/L)				Temperature (°C)		
Parameter	25	50	75	100	30	40	50
q_e (exp), (mg/g)	17.85	34.27	49.69	63.56	34.27	36.70	37.63
Pseudo-first-order kinetics							
$k_1 \times 10^{-2}$ (min^{-1})	3.109	3.201	2.326	3.132	3.201	3.731	3.293
q_e (cal), (mg/g)	5.6846	11.313	14.568	24.143	11.3135	14.5646	13.5456
r^2	0.9143	0.9092	0.9067	0.8987	0.9092	0.8786	0.9333
Pseudo-second-order kinetics							
$k_2 \times 10^{-4}$ (g/mg min)	94.4	48.7	28.8	21.2	48.7	42.9	40.8
h	3.3366	6.3492	7.9681	9.6899	6.3492	6.4977	6.4683
q_e (cal), (mg/g)	18.80	36.10	52.63	67.57	36.10	38.91	39.84
r^2	0.9977	0.9978	0.9956	0.9966	0.9978	0.9979	0.9978
Intra-particle-diffusion model							
K_{id}	0.5619	1.1035	1.6658	2.375	1.1035	1.273	1.3106
I	12.495	23.783	33.408	40.914	23.783	24.738	25.238
r^2	0.9738	0.98	0.9616	0.974	0.98	0.9794	0.9796

Table 3b
Calculated kinetic parameters for the adsorption of BR29 onto PPC at various initial dye concentrations and at various temperatures

	PPC						
	Initial dye concentration (mg/L)				Temperature (°C)		
Parameter	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
Intra-particle diffusion model							
K_{id}	0.8366	2.226	3.3758	5.2634	2.226	2.2218	2.2836
I	13.868	20.921	28.878	29.007	20.921	22.037	23.105
r^2	0.9628	0.9856	0.9716	0.9654	0.9856	0.9863	0.9808

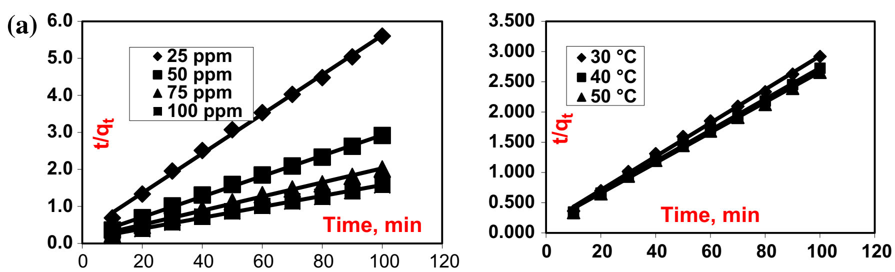

Fig. 7(a). Pseudo-second-order plot for the adsorption of BR 29 onto CSAC at various initial dye concentrations and at various temperatures.

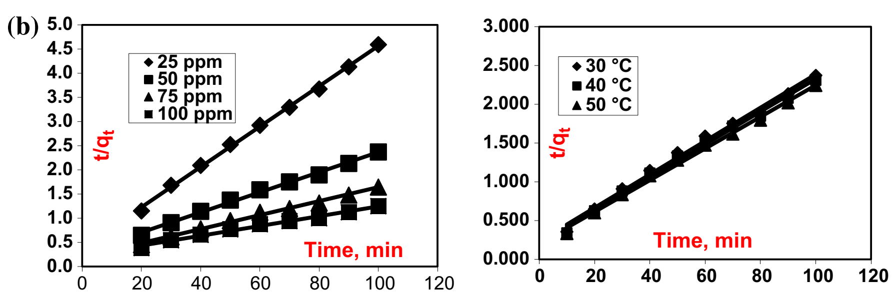

Fig. 7(b). Pseudo-second-order plot for the adsorption of BR 29 onto PPC at various initial dye concentrations and at various temperatures.

model to investigate whether the adsorption is intraparticle diffusion or not. According to this theory,

$$q_t = k_{d.t}^{1/2} \tag{3}$$

where k_d is the intraparticle diffusion rate constant and is calculated by plotting q_t vs. t½ at different initial dye concentrations and at different temperatures (shown in Figs. 8(a) and (b)).

All the plots have initial curved portion followed by an intermediate linear portion. The initial portion is related to mass transfer, and linear part is due to intraparticle diffusion. The values of K_{id} for all concentrations studied were determined from the slopes of respective plots, and the results were presented in Tables 3a and 3b. If the intraparticle diffusion is the only rate controlling step, the plot passed through the origin, if not the boundary layer diffusion controlled the adsorption to some degree [37]. But the plots obtained are not linear over the whole time range, implying that more than one process affected the adsorption, that is, the mechanism of removal of cationic dyes is complex and both surface adsorption as well as intraparticle diffusion contribute to the rate-determining step. Similar trend is also obtained for the adsorption of BG4, BV3 and BV10 onto TPAC [38].

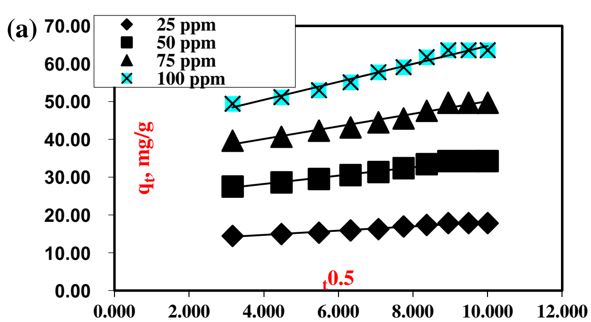

Fig. 8(a). Intraparticle diffusion plot for adsorption of BR 29 onto CSAC.

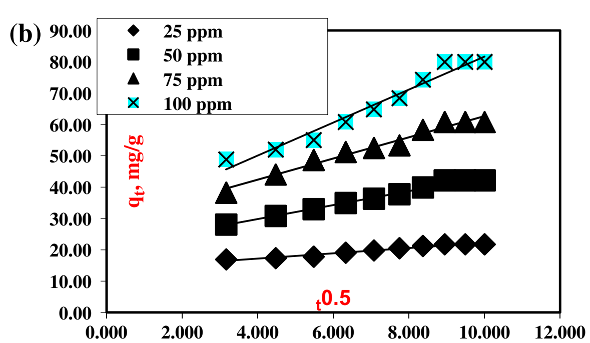

Fig. 8(b). Intraparticle diffusion plot for adsorption of BR 29 onto PPC.

3.8. Adsorption isotherms

The adsorption isotherm indicates the distribution of adsorption molecules between the liquid phase and the solid phase at constant temperature and at equilibrium state. To study the adsorption isotherm, the experimental data are interpreted using the two equilibrium models: the Freundlich and the Langmuir equations.

3.9. Langmuir isotherm

Langmuir model suggests a monolayer sorption and uniform energies of adsorption onto the surface, without interaction between the sorbed molecules [39]. The linear form of Langmuir is expressed as

$$\frac{1}{q_e} = \frac{1}{kC_e q_m} + \frac{1}{q_m} \tag{4}$$

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 $1/q_e$ vs. 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 (figure not shown) are given in Table 4. Langmuir adsorption capacity varies from 120.48 to 140.84 mg/g for CSAC and from 90.09 to 108.69 mg/g for PPC for the range of temperatures studied. An irregular trend was observed for both the adsorbents in the studied temperature. Furthermore, the values of r^2 suggests that the adsorption data fit poor to Langmuir isotherm.

The essential characteristics of the Langmuir equation can be represented in terms of a dimensionless separation factor, R_L, which is introduced by the following equation [40]

$$R_L = \frac{1}{1 + kc_i} \tag{5}$$

where C_i is the maximum initial concentration of adsorbate (mg/L). The value of R_L indicates the type of the isotherm whether it is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible

Table 4
Results of isotherm plots for the adsorption of BR29 onto CSAC and PPC

	CSAC			PPC		
	Temperature (°C)			Temperature (°C)		
Parameter	30	40	50	30	40	50
Freundlich isotherm						
n	1.29	1.35	1.41	1.62	1.89	2.03
k_f ($mg^{1-1/n} L^{1/n} g^{-1}$)	4.0290	4.8562	5.8196	11.3553	15.1390	18.6080
r^2	0.9983	0.9981	0.9948	0.9981	0.9953	0.9903
Langmuir isotherm						
Q_0 (mg/g)	140.8451	120.4819	126.5823	108.6957	90.9090	90.0900
b_L (L/mg)	0.0219	0.0299	0.0331	0.0883	0.1306	1.2293
r^2	0.9487	0.9370	0.8816	0.9369	0.8900	0.8866

($R_L = 0$). The values of R_L in the present investigation are found to be 0.2652 and 0.0715 for CSAC and PPC, respectively, which indicate that the adsorption of BR29 by CSAC and PPC is favourable.

3.10. Freundlich isotherm

The Freundlich model is often applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption [41]. The linear form of Freundlich isotherm is represented by

$$\log q_t = \log k + \frac{1}{n} \log c_e \quad (6)$$

where Q_e is the equilibrium dye concentration on the adsorbent (mg/L); C_e, the equilibrium dye concentration in solution (mg/L), K is the Freundlich constant (mg/g (L/mg) $1/n$) which represents the adsorption capacity and n is the heterogeneity factor. Value of $n > 1$ represents that the adsorption process is favourable. A plot of log q_e vs. log C_e indicates a straight line of slope $1/n$ and an intercept of log K (shown in Figs. 9(a) and (b)). The values of Freundlich parameters with the nonlinear correlation coefficients (r^2) are listed in Table 4.

The Freundlich constant K_f increases with the increase of temperature. The value of Freundlich exponent n is 1.35 for CSAC and 1.85 for PPC which is in the range of $n > 1$, indicating a favourable adsorption and multilayer coverage process of sorption by both the adsorbents. The r^2 value for Langmuir isotherm is 0.9224 for CSAC and 0.9045 for PPC obviously lower than the Freundlich isotherm for CSAC which is 0.9971 and for PPC which is 0.9946. From the Table 4, it is concluded that the adsorption of BR 29 onto CSAC and PPC match Freundlich isotherm model.

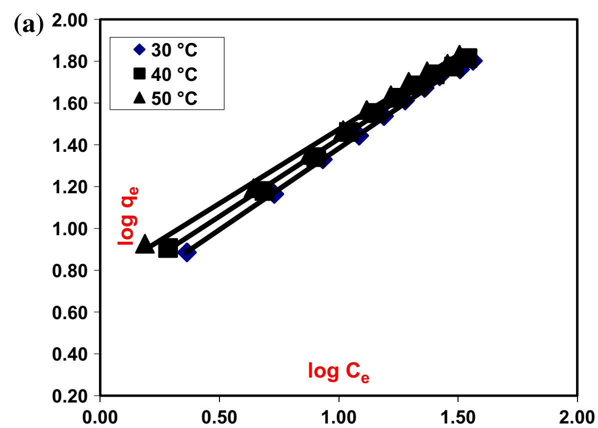

Fig. 9(a). Freundlich adsorption isotherm plot for the adsorption of BR 29 dye onto CSAC.

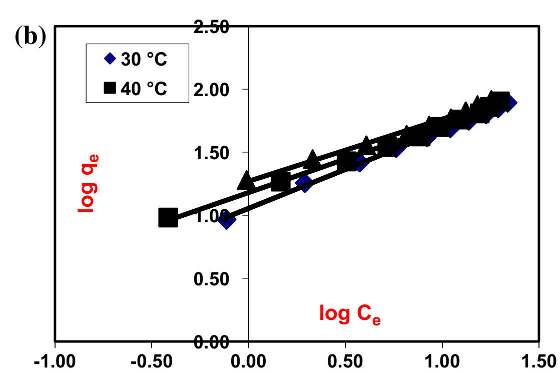

Fig. 9(b). Freundlich adsorption isotherm plot for the adsorption of BR 29 dye onto PPC.

Thus, Freundlich model is more appropriate to explain the nature of adsorption rather Langmuir model that shows poor fit.

Table 5
Comparison of the Langmuir sorption capacity (q_m in mg/g) of different sorbents for different direct dyes

Sorbent	q_m (mg/g)	Dyes	References
Present study		BR 29	–
Activated carbon from *C. sebestena* fruit.	140.84		
Polypyrrole polymer composite obtained from fruit sawdust from *C. sebestena.* (PPC)	108.69		
Activated carbon from *Euphorbia antiquorum* L	166.67	BR 29	[42]
Dried activated sludge	224.72	BR 29	[43]
Activated sludge	285.71	BR 18	[44]
Animal bone meal	24.31	BR 46	[45]
Sawdust coated with polypyrrole	34.36	MB	[46]

Table 6
Thermodynamic parameters for the adsorption of BR29 onto CSAC and PPC

	CSAC			PPC		
Temperature (°C)	ΔH° (kJ/mol)	ΔS° (kJ/K/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K/mol)	ΔG° (kJ/mol)
30	12.491	0.0505	−2.8105	30.99	0.1206	−5.5518
40			−3.3155			−6.7578
50			−3.8205			−7.9638

The maximum adsorption value q_m (mg/g) obtained in this study was compared with those of the other sorbents for basic dye category adsorption (Table 5). The q_m value obtained is lower than that of the other adsorbents presented in Table 5 with the same type of BR29 dye. At the same time, q_m value is high when compared to the other dyes with different adsorbents. Hence, the results of this comparison show that CSAC and PPC have great potential as sorbents for BR 29 adsorption and can compete favourably with the other sorbents that have been studied.

3.11. Thermodynamics of adsorption

Thermodynamic parameters provide in-depth information of inherent energetic changes associated with adsorption, and so, these parameters should be accurately evaluated. Langmuir isotherm equation is applied to calculate the thermodynamic parameters as follows:

$$\ln k_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} \quad (7)$$

where k_L is the Langmuir equilibrium constant and ΔH° and ΔS° are the standard enthalpy and entropy changes of adsorption, respectively.

Thermodynamic parameters such as ΔH°, ΔS° and ΔG° are determined from the slope and intercept of Van't Hoff's plot of ln k_L vs. $1/T$ (as shown in Figs. 10(a) and (b)), and the results are given in Table 6. The ΔG° values indicate that the adsorption of BR29 is spontaneous and thermodynamically favourable. The positive ΔH° values indicate that the adsorptions of BR29 dye onto CSAC and PPC were an endothermic process which is supported by the increase of adsorption of the dye with increase in temperature. Furthermore, positive values of ΔS° suggest good affinity of the dye towards the adsorbent, and the adsorption is spontaneous in nature [47]. Generally, ΔG° for physisorption is between −20 and 0 kJ/mol and for chemisorptions, it is between −80 and −400 kJ/mol [48].

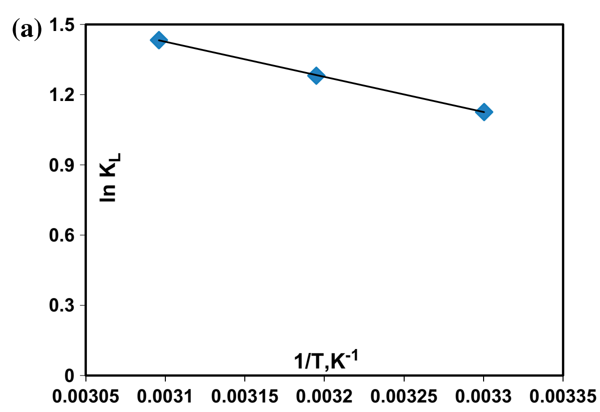

Fig. 10(a). Van't Hoff's plot for the adsorption of BR 29 onto CSAC.

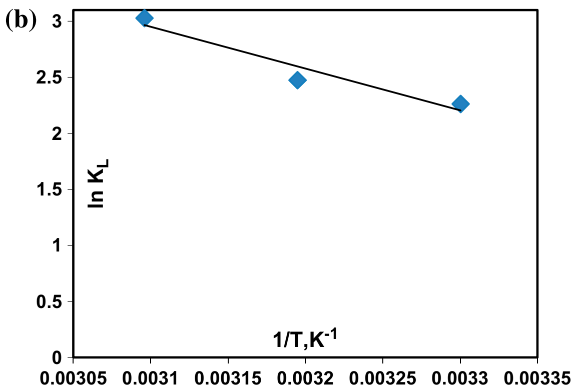

Fig. 10(b). Van't Hoff's plot for the adsorption of BR 29 onto PPC.

From Table 6, it confirmed that the adsorption of BR29 onto CSAC and PPC is physisorption.

3.12. Desorption studies

Desorption studies as a function of pH are conducted to analyse the possibility of reuse of both the adsorbents for further adsorption and to make the process more economical. For this study, 100 mg of the dye-loaded carbon and dye-loaded PPC is agitated above the equilibrium time with 100 ml of the double distilled water of various pH and the desorbed dye is estimated as stated in the adsorption studies [49].

A significant amount of dye is desorbed from the dye-loaded CSAC and PPC. Maximum desorption of 16.6% for CSAC and 40.5% for PPC is observed at the pH range of 2–4. Desorption decreases with the increasing pH. High percentage of desorption at lower pH is due to the presence of more amount of competitive H^+ ions.

4. Conclusion

In this investigation, Activated Carbon (CSAC) and PPC were prepared from the fruit of plant material *C. sebestena* for the adsorption of BR29 from its aqueous solution. The amount of BR 29 adsorption has increased from 17.85 to 63.56 mg/g for CSAC and from 21.78 to 79.96 mg/g for PPC with an increase in the initial concentration from 25 to 100 mg/L. The percentage of dye removal is high in PPC when compared to CSAC due to the surface modification of the sawdust by the polymer polypyrrole which is confirmed by IR study. The kinetic data reveal that the sorption of BR29 by CSAC and PPC follows second-order kinetics. Equilibrium isotherm analyses reveal that thesorption of BR29 by CSAC and PPC follows Freundlich model with high correlation coefficient as compared to Langmuir model. The determination of thermodynamic parameters indicates the spontaneous and endothermic nature of adsorption process in both the cases. Thus, from the kinetic, isotherm and thermodynamic analyses, it is found that PPC can be effectively and efficiently used for the removal of basic dye BR29 from aqueous solution as compared to that of CSAC.

Nomenclatures

CS	—	*Cordia sebestena*
AC	—	activated carbon
CSAC	—	*Cordia sebestena* Activated Carbon
PPC	—	polypyrrole polymer composite
BR29	—	Basic Red 29
SEM	—	scanning electron microscope
FTIR	—	Fourier transform infrared
SD	—	sawdust
q_t and q_e	—	amount of dye adsorbed (mg/g) at time t(min) and at equilibrium
k_1	—	pseudo—first order rate constant (min^{-1})
k_2	—	pseudo—second order rate constant (g/mg min)
h	—	initial adsorption rate (mg/g/min)
r^2	—	correlation coefficient
k_d	—	intraparticle diffusion rate constant
C_e	—	equilibrium concentration (mg/L)
q_m	—	maximum adsorption capacity for a monolayer (mg/g)
R_L	—	dimensionless separation factor
C_i	—	maximum initial concentration of adsorbate (mg/L)
k_L	—	Langmuir equilibrium constant
ΔH°, ΔS° and ΔG°	—	standard enthalpy, entropy and free energy changes of adsorption

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