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Novel synthesis of *Chrysanthemum indicum* flower as an adsorbent for the removal of direct Congo red from aqueous solution

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ABSTRACT

The present study focused on preparation of thermally activated carbon from *Chrysanthemum indicum* flower and investigated its effectiveness on removal of direct congo red (DCR) dye from aqueous solution by batch mode. The *Chrysanthemum indicum* flower carbon (CIFC) was prepared and characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The batch adsorption study showed that the amount of adsorption depends on various physicochemical parameters, such as solution pH, adsorbent dose, contact time, dye concentration and temperature. Further, pseudo-second-order model was fitted to examine the adsorption kinetics and mechanism of adsorption. Equilibrium data was fitted with Langmuir and Freundlich adsorption isotherm models and thermodynamic parameters were calculated such as $\Delta G°$, $\Delta H°$, and $\Delta S°$. The maximum adsorption capacity of 43.47 mg g^{-1} was obtained for direct congo red. Through this study it was found out that the CIFC is a good and a cheap precursor to produce an effective adsorbent and alternative to commercial-activated carbon.

Keywords: Chrysanthemum indicum flower; Direct Congo red; Adsorption Kinetics; Isotherm

1. Introduction

Water is essential for all living organisms. But, the recent industrial revolution is defiling the water bodies through the effluents. Major sources of water pollution are dyes, heavy metals, phenols, etc. Everyday two million tons of wastewater is directly discharged into the water bodies [1–3]. Particularly, textile industries are using high volume of water for numerous processes like bleaching, dyeing, printing and finishing process [4]. Its annual production is 7×10^5 tonnes of dyes from which 10% are discharged into the natural water bodies, it causes carcinogenic effects, eye injuries, skin irritation, dermatitis for living organism [5–7], and affect the aquatic organisms (flora and fauna) [8,9].

Dyes are used widely and it causes serious environmental problems. Specifically, the direct dyes are highly utilized in numerous industries like textile, rayon, paper and leather. These dyes have more colours and they react with the cellulosic fibre to form covalent bonds; easily available in the market and they are problematic to degrade because they undergo hydrolysis of the sulfone group making it unreactive to the cellulose [10]. Particularly, the DCR is known as human carcinogen and its exposure causes skin allergy; this dye also considered as toxic substance [11]. The removal of DCR from wastewater/aqueous solution was considered an environmental

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challenge and it has to be removed from the productive environment. However, in the past many conventional techniques were applied for dye, heavy metal, and phenolic compounds removal. There are membrane filtration, ultra-filtration, coagulation, flocculation, oxidation or ozonation, electrolysis processes, reverse osmosis, biosorption and adsorption [12–18]. Among all the adsorption methods one of the best is physicochemical method which is an efficient, reliable and economic viable technique for the removal of hazardous substances [19–21]. Numerous studies were conducted to prepare activated carbon such as coir pith [22], H_2SO_4 coir pith [23], pomegranate peel [24], micro algae [25], paper sludge [10], pine leaves, pine cone, raw mango seed, and apricot seed, etc., [26] which were utilized for the removal of environmental pollutants (heavy metals, dyes and phenol compounds) [9].

Mostly the activated carbons were prepared form chemical activation. But a limited investigation is available for thermal activated adsorbent. The chemically modified adsorbents are economically expensive when compared to the thermal activated carbon. This thermal activated carbon is widely suitable for industrial process.

The present study focussed on thermal activation of waste *Chrysanthemum indicum* flower biomass to utilize as an adsorbent for the removal of DCR from the aqueous system. This *Chrysanthemum* is perennial plant, growing up to 0.6 meters. It blossoms from August to October. The whole plant has many medicinal uses however the flower is mostly used for garland making in India. *Chrysanthemum indicum* flowers are highly used and wasted in Indian temples. Thus we tend to use these flowers for this investigation for the preparation of activated carbon and it was applied for textile waste water treatment in addition it has high efficient surface area for adsorption process [27].

2. Materials and methods

2.1. Preparation of CIFC absorbent

The *Chrysanthemum indicum* flowers were collected from local temples in and around Salem district (Latitude – 11.7345° N, Longitude – 78.2020° E), Tamil Nadu, India. *Chrysanthemum indicum* flowers were rinsed in the deionized water for the removal of impurities and then dried at 100°C in hot air oven for six hours. The flower carbon was prepared as follows: the dried flowers were sealed in an airtight container and transferred to muffle furnace (Muffle furnace SERVO, India) for thermal activation at 600°C for one hour. Finally, activated material was collected and cooled at room temperature to sieve for further use.

2.2. Preparation of dye stock

The stock solution was prepared for 1000 mg L^{-1} of DCR by dissolving 1 g of dye in 1 L of deionized water and it is stored in amber bottle intended for avoiding photo degradation. The different concentrations of working solutions were prepared from the stock solution. The working solutions absorbance measurement was carried by using UV-Vis spectrophotometer (Shimadzu, UV-1800, Japan). The maxima absorbance of dye clearly obtained at 499 nm with different concentrations.

2.3. Characterization of CIFC

The prepared CIFC was characterized for its basic properties such as pH, mechanical moisture content, bulk density, ash content, specific gravity, porosity and zero-point charge (pH_{zpc}). The dye loaded and unloaded CIFC morphology was subjected by scanning electron microscopy (SEM, JSM-6400 JEOL (Japan Electron Optics Ltd., Japan)). Crystal structure analysis of CIFC was determined through X-ray diffraction (Rigaku X-ray diffractometer, Japan) in the 2θ-range from 20 to 80° with a step size of 0.02° and Fourier transform infrared (FTIR) spectra (Perkin-Elmer FTIR spectrophotometer, Norwalk, USA) was used to analyze the functional group of CIFC in the scanning range of 4000–400 cm^{-1} with the diffuse reflectance mode of resolution at 4 cm^{-1} in KBr pellets.

2.4. Removal efficiency of the obtained carbon and removal optimization

To evaluate adsorption properties of CIFC for DCR, a series of adsorption experiment, including adsorption kinetics, isotherm and thermodynamics were conducted. The batch mode adsorption isotherms were obtained with different weights (50–250 mg), initial concentrations (20, 40, 60, 80, 100 mg L^{-1}), at solution pH (2–10) and at different temperatures (308 K, 318 K and 333 K). The stock solution of DCR (1000 mg L^{-1}) was prepared by mixing DCR in deionized water. The desired concentration of DCR was prepared by diluting their respective stock solution of DCR. Each experiment was carried out in 100 ml conical flask filled with specific concentrations of dye solution with adsorbent and agitated at 160 rpm using a shaking incubator at predetermined time intervals. The samples were removed from shaker at predetermined time intervals and supernatant solution was separated from the adsorbent by centrifugation at 2,500 rpm for 15 min. The absorbance of supernatant solution was measured at 499 nm using UV–visible spectrophotometer. The percent removal of adsorption was calculated by Kumar et al. [23] equations.

The batch mode desorption study was carried out in used adsorbent for de-adsorption of the adsorbate were separated from the solution by using filter paper. The spent adsorbent was agitated for equilibrium time with 25 ml of various strengths of 1 N NaOH, 1 N HCl and deionized water. The desorption is calculated by using Kumar et al. [23] equations.

3. Result and discussion

3.1. Adsorbent characterization

The physico-chemical properties of CIFC are presented in Table 1. The pH of the CIFC is basic in nature [28, 29]. This may due to the presences of residual salts and it was highly suitable for industrial wastewater treatment. Porosity is the main factor for increasing the adsorptive power and it has interrelated to the bulk density and specific gravity of CIFC. The bulk density indicates that the fibre content present in the activated material [30,31], the minimum level moisture content was no effect on activated carbon; assume it contained prominent level it gives additional weight during the treatment process. Inorganic constituents were associated with carbon for reason of ash content. This data indicates ash content of activated carbon is 30% of inorganic content and fixed carbon of 70% [32].

Additionally, pH_{zpc} is the important parameter for activated carbon. The CIFC zero charge was found at pH 8.5 as shown in Fig. 1a. Basically the surfaces of carbon were acidic at less than pH 8.5 and alkaline at greater than pH 8.5. Further, it was evident that adsorbent has better adsorption capacity in the acetic pH range. The treatment of aqueous solution, its higher uptakes obtained at pH < 8.5 can be attributed to the electrostatic interaction between the positively charged carbon. Simultaneously, negative charge (pH > 8.5) contains lower uptakes [33]. The prepared CIFC before and after adsorption of dye were characterized for phase analysis in the 2θ range from 20° to 80° by XRD. The XRD pattern of CIFC and DCR adsorbed CIFC are shown in Fig. 1b. As per the review of literature the occurrence of two broad peaks conforming activated carbon are crystal structures [34].

Table 1
Physico-chemical properties of CIFC

Parameter	Activated carbon
pH	9.65
pH_{zpc}	8.5
Bulk density (g/cm^3)	0.14
Porosity (%)	0.76
Specific gravity	0.08
Moisture content (%)	8.75
Ash (%)	30

The FTIR spectrum of CIFC was an absorption band clearly, shown Fig. 1c, N–H stretching group at 3415 cm^{-1} (broad spectrum). The band at 2931 cm^{-1} is related to asymmetric and symmetric stretching of CH_2 group. Scissor bending of the NH_2 group can be observed at 1630 and 1405 cm^{-1}. The band at 1005 cm^{-1} can be assigned to the C-N stretch of amide or amine group. The bands in the region 750–800 cm^{-1} can be attributed to aromatic C-H stretching vibrations. The Bands of 702 cm^{-1} are indicated C-C stretching group. The same as Fig. 1c is shown FTIR spectrum of DCR adsorbed CIFC, the intense absorption band at 3376 cm^{-1} related to O-H bond stretching mixed with the NH_2 group (broad spectrum). Another scissor band of the NH_2

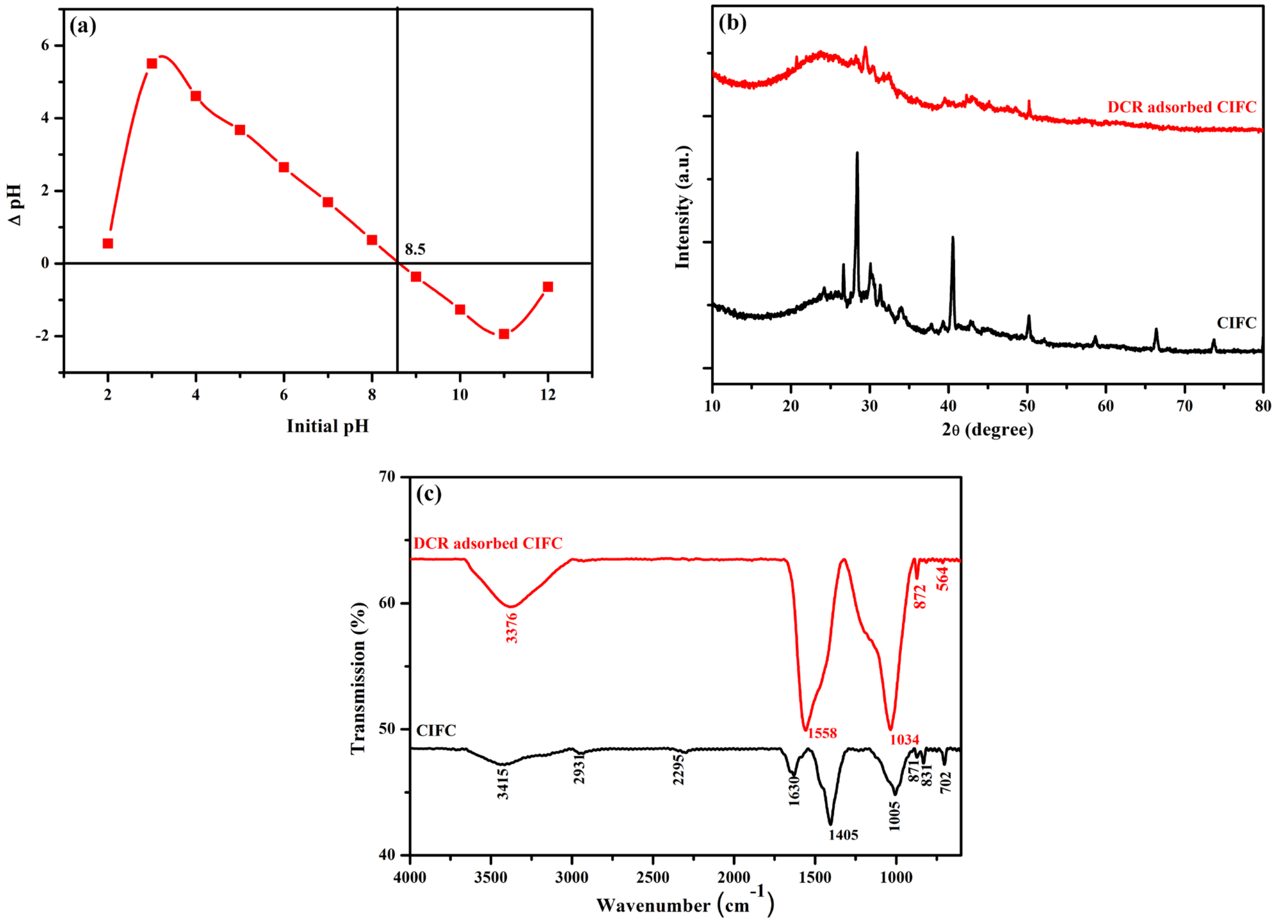

Fig. 1(a) Determination of zero-point charge, (b) XRD pattern and (c) FT-IR spectrum of CIFC and DCR adsorbed CIFC.

group observed at 1558 cm^{-1} (sharp band). The band at 1034 cm^{-1} can be assigned to the C-N stretch by amide or amine groups. The bands at 872 and 564 cm^{-1} can be attributed to aromatic C-H stretches and C-C stretching groups.

The prepared CIFC was visually observable powder. Microstructure structure and the morphologies of CIFC were further examined by SEM. Greater number of pores, grater the adsorption of dye onto the CIFC because adsorption also depends on the number of pores of the adsorbent. Fig. 2 shows unloaded and loaded adsorbent morphological changes onto the adsorbent surface. On the surface of DCR loaded CIFC formation pores are filled with DCR. Safa and Bhatti [35] stated difference between the untreated and dye treated carbon surface morphology. Akar et al. [36] reported olive pomace biomass surface morphology RR 198 dye presence. These flower carbon surfaces were also similar to the confirmed earlier reports [37,38].

3.2. Effect of pH study

The pH is one of the most important parameters of adsorption study. In this investigation, adsorption of DCR ions on CIFC was evaluated with a pH range of 2–10 by fixing the concentration of adsorbent dosage 100 mg for different initial concentrations of adsorbate as 20–100 mg L^{-1}. The result shows (Fig. 3a) adsorption capacities of DCR increases significantly with the increase of pH from 2 to 4 and there is a small decrease with a range of 4–10. The adsorption maximum was observed at 97.5 and 90.5% of CIFC. Similar reports were previously stated for adsorption of Congo red (CR) at a lower pH range on *phoenix dactylifera* seeds [39] and coir pith [40]. The mechanism of adsorption is decreased by increasing the initial concentration of dye from 20 to 100 mg L^{-1}. Since the optimum pH for DCR adsorption by CIFC was found higher at pH 2.

3.3. Effect of the sorbent dosage

The sorbent dosage was another important parameter; it controls the capacity of adsorbent. The effects of CIFC dose on the adsorption of DCR from aqueous solutions were investigated using various adsorbent doses (50–250 mg) at different concentrations DCR (20 and 100 mg L^{-1}). The investigation results are presented in Fig. 3b. The removal

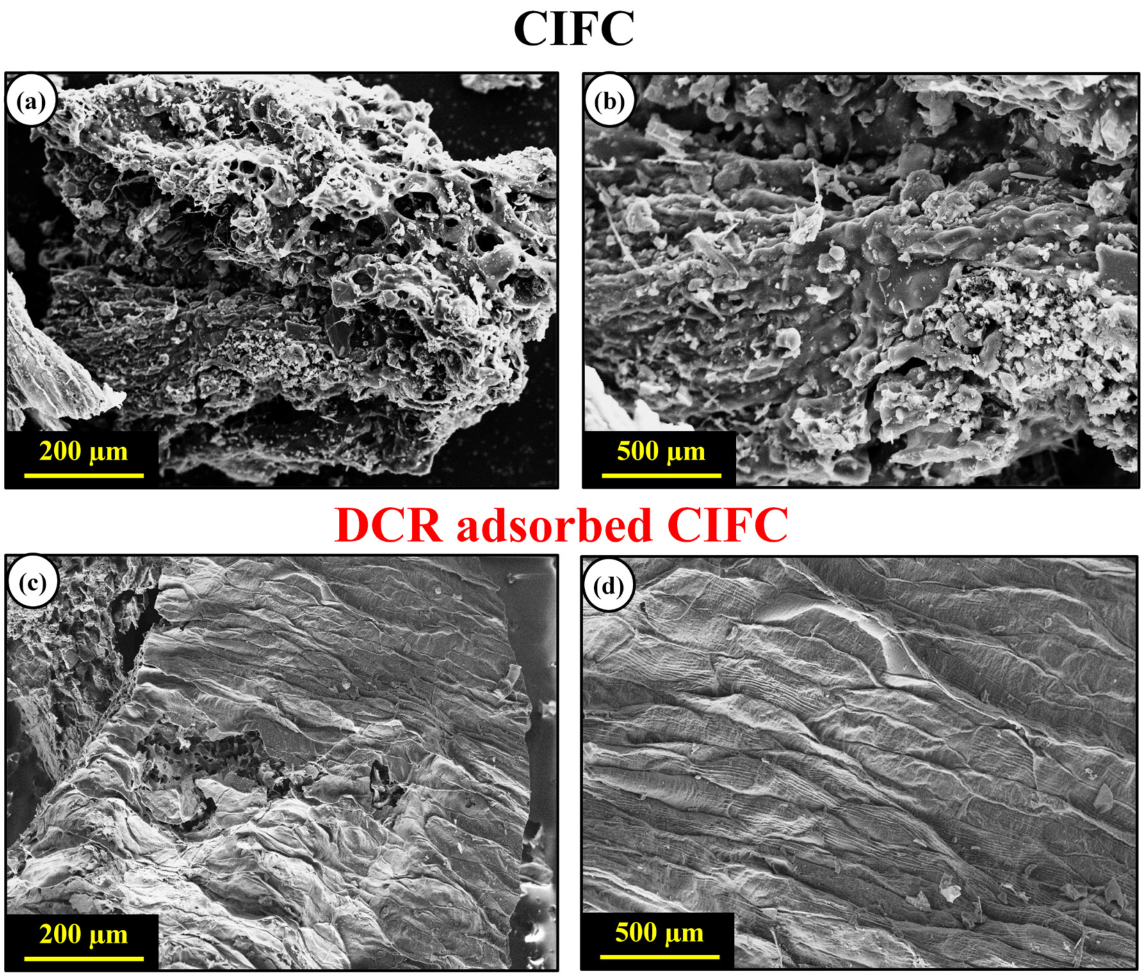

Fig. 2. SEM image of CIFC unloated DCR (a, b), CIFC loaded DCR (c, d).

efficiency of DCR by CIFC increased sharply as the sorbent dose increased from 50 to 100 mg, then reached an almost constant value. It was evident that DCR removal increased proportionally with dose which is due to the availability of greater surface area of the adsorbent [39]. Therefore, 100 mg was optimized and it economically viable dose for environmental pollutant removal [41].

3.4. Effect of contact time and temperature

The effect of contact time on the adsorption was investigated with different concentration of DCR (20–100 mg L^{-1}) at an optimized adsorbent dose from 0 to 180 min by increasing temperature. Figs. 4a–c show the effect of contact time on the removal of DCR at different temperatures 310, 318 and 333 K, respectively. There was a slight variation in the different temperature removal; the adsorption level increased with an increasing temperature. This process indicates an endothermic reaction of CIFC.

3.5. Adsorption kinetics

The adsorption kinetics of DCR was adsorbed on CIFC and found that the removal rates of DCR were very rapid during the initial stages of adsorption process. It has been proposed to clarify the adsorption kinetic mechanism. To investigate the mechanism of DCR adsorption onto CIFC, pseudo first-order (PFO) and pseudo second-order kinetic (PSO) model has been examined [42,43].

The rate expression for PFO reaction can be described as follows [44]:

$$\log\left(q_e - q\right) = \log q_e - \frac{k_1 t}{2.303} \qquad (1)$$

where q_e and q are the amount of DCR adsorbed (mg g^{-1}) at equilibrium and at time t (min^{-1}), respectively, k_1 is the rate constant of PFO model (min^{-1}). The values of the q_e and k_1 were obtained from the slope and intercept of the plots of log ($q_e - q$) vs. t for different concentration of DCR at different temperature.

The rate expression for PSO reaction can be described as follows [45]:

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^{\,2}} \qquad (2)$$

where K_2 is the PSO rate constant (g mg^{-1} min^{-1}). The values of K_2 and q_e were estimated from the plots of t/q vs. t for different concentration of DCR at different temperature.

Both PFO and PSO kinetic models were applied for the adsorption of DCR onto CIFC and the results are shown in Table 2. The results noticed CIFC adsorption follows the PSO kinetic model, so the mechanism of adsorption process can be described as chemisorption. The CIFC material was already reported, adsorption follows PSO [27]. Most of the good adsorbent materials followed PSO, for example coir pith [39], *Borassus aethiopum* flower carbon [43], and *Cortaderia selloana* flower spikes [46]. Comparatively, other material to this material kinetics correlation is highly fitted with PSO.

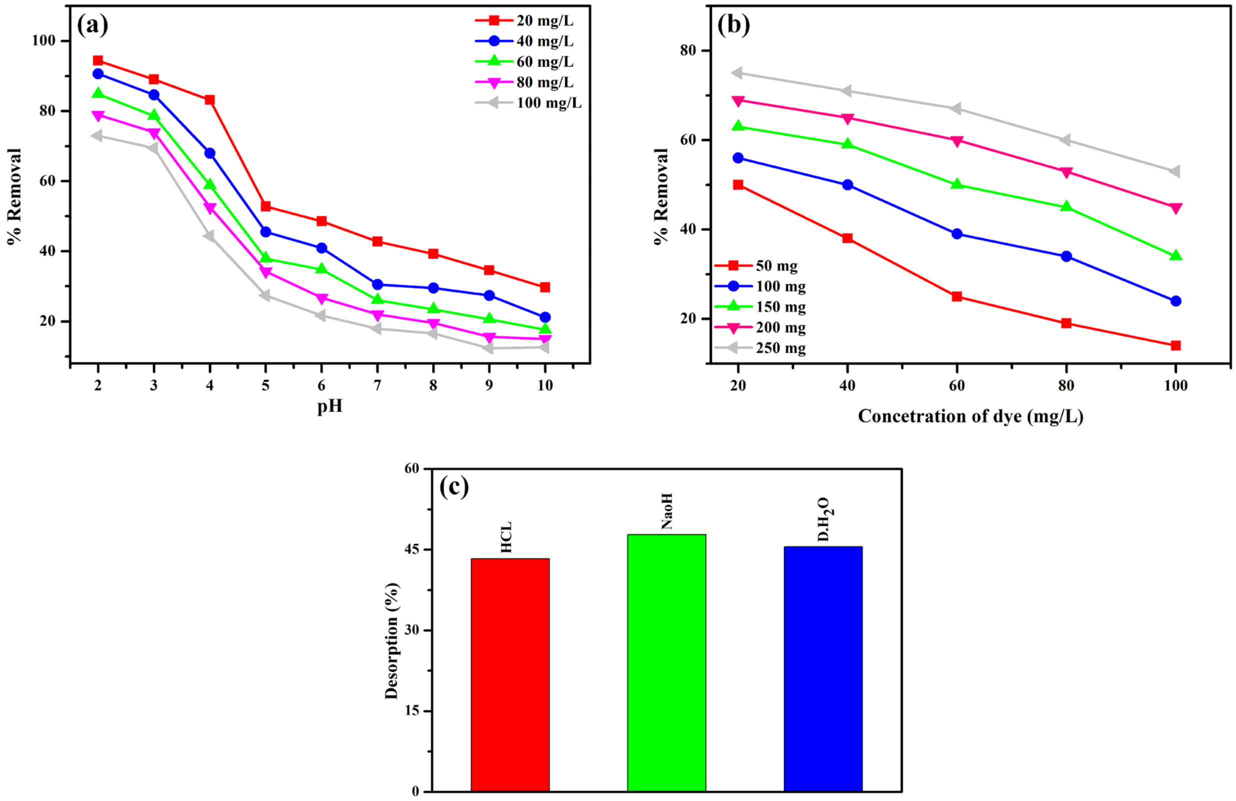

Fig. 3. (a) Effect of pH, (b) adsorbent dosage and (c) Desorption of DCR.

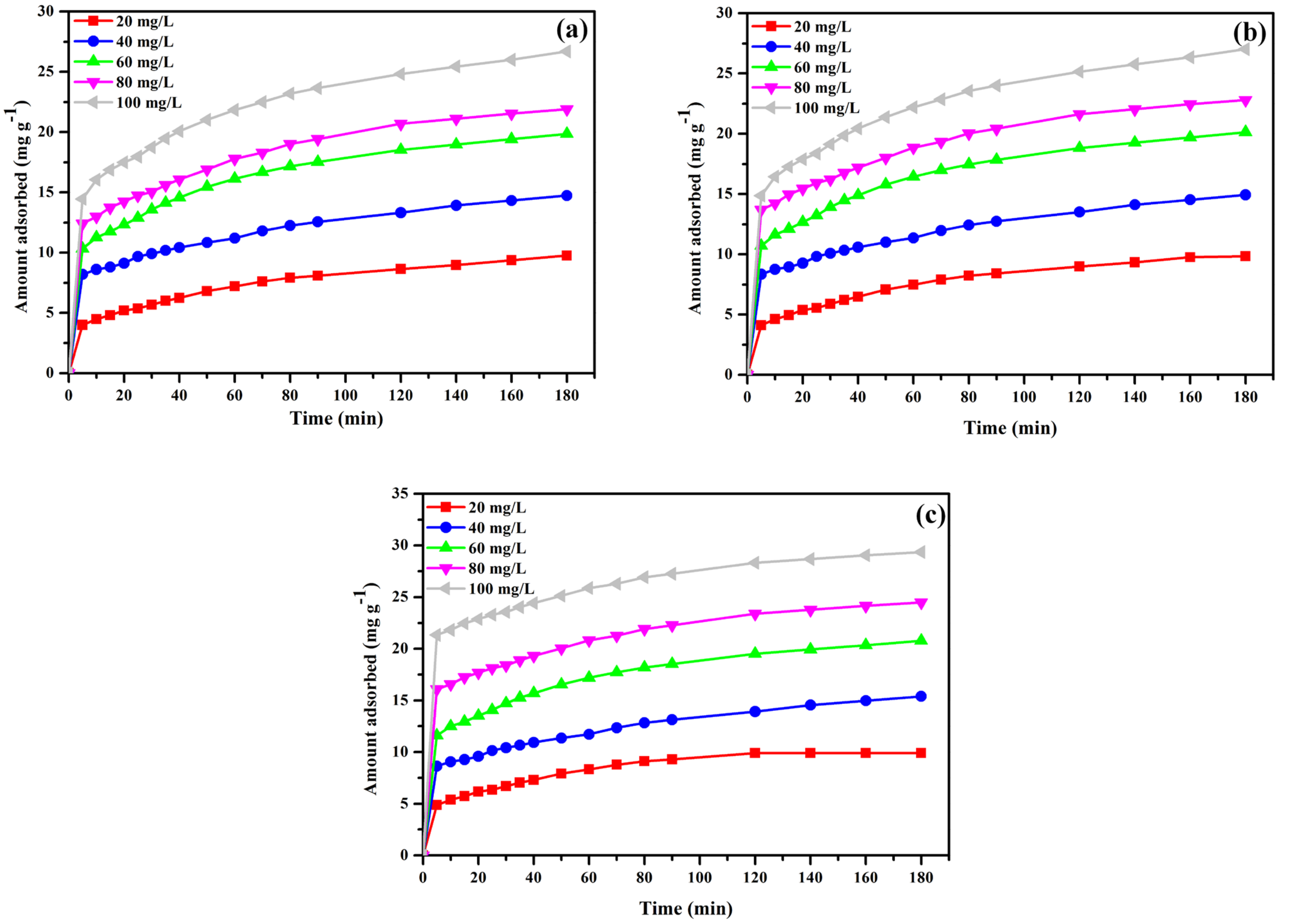

Fig. 4. Contact time and dyes initial concentration at different temperature (a) 310 K, (b) 318 K and (c) 333 K.

Table 2
Adsorption kinetic parameters of DCR onto CIFC

Temperature (K)	Concentration (mg L^{-1})	q_e (exp)(mg g^{-1})	First order kinetic model			Second order kinetic model		
			K_1 (min^{-1})	q_e cal (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e cal (mg g^{-1})	R^2
310	20	6.24	0.06	3.68	0.92	0.03	6.57	0.99
	40	10.83	0.05	4.03	0.95	0.03	10.98	0.99
	60	16.12	0.04	8.55	0.94	0.01	16.66	0.99
	80	18.29	0.03	8.87	0.90	0.01	18.86	0.99
	100	22.48	0.04	11.32	0.95	0.007	23.25	0.99
318	20	6.21	0.06	3.25	0.96	0.04	6.45	0.99
	40	11.35	0.04	4.53	0.95	0.02	11.62	0.99
	60	16.44	0.04	9.07	0.94	0.01	16.94	0.99
	80	20.03	0.02	8.07	0.96	0.01	19.60	0.99
	100	22.84	0.04	11.2	0.95	0.007	23.81	0.99
333	20	7.04	0.02	4.81	0.98	0.04	7.24	0.99
	40	12.35	0.05	3.36	0.96	0.01	12.34	0.99
	60	17.72	0.04	9.14	0.94	0.009	18.51	0.99
	80	21.27	0.03	7.85	0.90	0.01	21.73	0.99
	100	25.88	0.03	6.15	0.95	0.02	25.64	0.99

3.6. Adsorption isotherms

The adsorption equilibrium data were investigated by Langmuir and Freundlich isotherm model equations for DCR adsorbed by CIFC with different temperatures [47].

In the present investigation equilibrium data for adsorption of DCR on to CIFC were analyzed by considering Langmuir and Freundlich isotherm models. The Langmuir isotherm equation in a linear form [7] represented as:

$$\frac{c_e}{q_e} = \frac{1}{q_o b} + \frac{c_e}{q_o} \tag{3}$$

The Langmuir plot (C_e/q_e vs. C_e) for DCR adsorption at different temperatures gives a straight line and the value of Q_o and b is Langmuir constants related to adsorption efficiency and energy of adsorption are shown in Table 3 and Figs. 5a–c, respectively [48]. The R^2 value of 0.94 indicated that the adsorption data of DCR on to the CIFC at different temperatures calculated were best fitted to the Langmuir isotherm model. Furthermore, Langmuir isotherm can also be expressed in terms of a dimensionless separation factor (R_L), defined as:

$$R_L = \frac{1}{1 + bc_o} \tag{4}$$

where b and C_0 are the Langmuir constant and initial concentration of dye, respectively. The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L>$ 1), linear (R_L = 1), favourable (0 <R_L< 1) or irreversible (R_L = 0). Value of R_L was found in DCR presented in Table 2. From the experimental data represent R_L value (0–1) clearly showed favorable of adsorption process.

Pure empirical form of Freundlich isotherm was explaining the adsorption of dye molecules onto a heterogeneous system. The Freundlich isotherm was represented as [49]:

$$\log q_e = \log k_f + \frac{\log C_e}{n} \tag{5}$$

From the intercept and slope of a linear plot of log q_e vs. log C_e (Figs. 5a–c), the values of K_f and $1/n$ can be determined (Table 3), respectively. The Freundlich constant should have a value in the range of 1–10 which again proved that the adsorption was favorable [50].

3.7. Adsorption thermodynamics

Thermodynamic studies were carried out to infer the mechanism of adsorption on CIFC with different temperatures (310, 318 and 333 K) at their respective optimum adsorbent dose at different dye concentrations (20–100 mg L^{-1}).

Thermodynamic parameters such as standard free energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$) of adsorption were calculated using the following equations:

$$\Delta G° = -RT \ln K_c \tag{6}$$

where R is the universal gas constant (8.314 J mol^{-1} K), and K_c is the equilibrium constant (L mol^{-1}) and T is the temperature (°K).

The values of above mentioned thermodynamics parameters determined by Van't Hoff equation [48]:

Table 3
Langmuir and Freundlich constant for the adsorption of DCR on CIFC

Temperature (K)	Concentration (mg L^{-1})	Langmuir isotherm				Freundlich isotherm		
		Q_o (mg g^{-1})	b (L mg^{-1})	R_L	R^2	K_f(mg$^{1-1/n}$/L$^{1/n}$ /g)	n	R^2
310	20	38.46	0.02	0.67	0.94	1.7	1.55	0.98
	40			0.51				
	60			0.41				
	80			0.34				
	100			0.29				
318	20	41.66	0.02	0.68	0.99	1.6	1.47	0.98
	40			0.52				
	60			0.42				
	80			0.35				
	100			0.30				
333	20	43.47	0.02	0.63	0.96	2.3	1.61	0.99
	40			0.46				
	60			0.36				
	80			0.30				
	100			0.25				

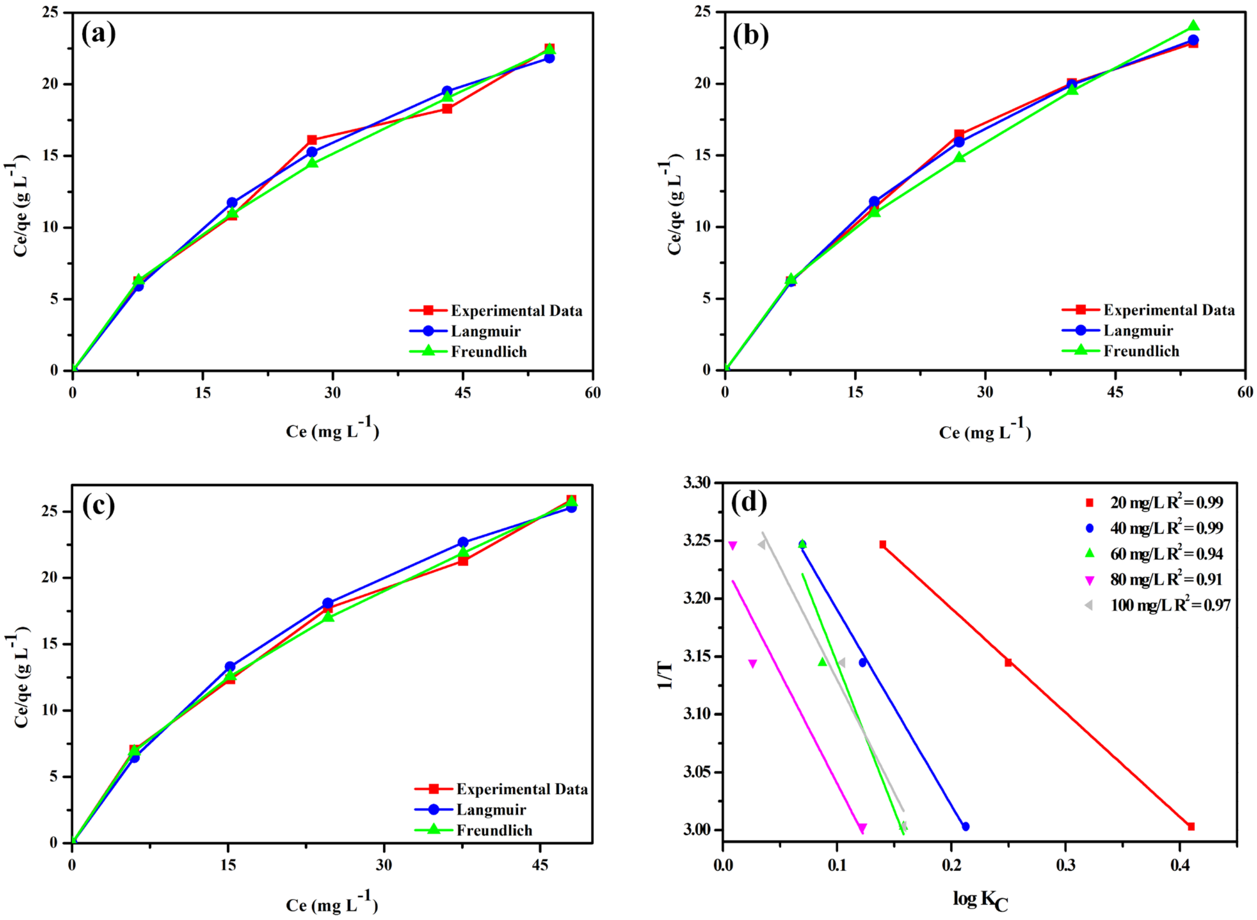

Fig. 5. Adsorption of DCR at different temperature isotherm comparison ((a) 310 K, (b) 318 K and (c) 333 K) and (d) Van't Hoff plot for DCR adsorption on CIFC.

$$\log_{10} K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{7}$$

where the values of ΔH° and ΔS° were obtained from the slope and intercept of the plot of ln K_c vs 1/T (Fig. 5(d). From Table 4, the negative values of ΔG° and positive value of $\Delta H^\circ$and ΔS° for the adsorption of DCR on both CIFC indicate the spontaneous, endothermic nature of the process and it suggest increasing the randomness of adsorbent–adsorbate interface [51,52].

Table 5 shows the comparison of maximum dye adsorption capacity with different adsorbents. It can be noted from the table that adsorption capacity of CIFC is significant and comparably it is higher than earlier reports for removal of Congo red from aqueous solution.

3.8. Batch mode desorption study

A batch mode desorption experiment was carried out at ambient temperature, adding 1 N NaOH, 1 N HCl and DW in spending adsorbent for recovering the adsorbent. Desorption efficiency is shown in Fig. 3c, highest percent desorption of 48% was obtained in 1 N NaOH at 60 min. Dye loaded adsorbent were utilized as a replacement of cement proportions for the preparation of cement blocks, thereby avoiding the problem of sludge disposal [61,62].

4. Conclusion

In summary, CIFC was employed as a low-cost adsorption material to remove the DCR from aqueous solution at different temperature. The experimental parameters concluded that the optimum removal of DCR via adsorption over CIFC at enter the range pH from 2 to 4, adsorbent dosage of 2 g L^{-1} and contact time 60 min at any temperature (310 K, 318 K and 333 K). The present removal was decreased with increasing in dye concentration. The kinetics, isotherm and thermodynamic study reveal that the experimental adsorption data fitted well with PSO and Langmuir and Freundlich isotherm models and increasing temperature favor for adsorption process were found spontaneous and endothermic in nature. Desorption studies show that the ion-exchange mechanism seems to be the major mode of adsorption for DCR onto CIFC. The CIFC was more suitable for the recovery of adsorbate and there was a possibility of reuse of the adsorbent. This result shows that CIFC is effective and efficient eco-friendly adsorbent for the removal of environmental contaminates.

Table 4
Thermodynamic parameters for DCR adsorption on CIFC

Concentration (mg L^{-1})	Temperature	$-\Delta G^\circ$ (kJ mol^{-1})	ΔS° (kJ $mol^{-1}K^{-1}$)	ΔH° (KJ mol^{-1})	R^2
20	310	–0.82	64.54	17.25	0.99
	318	–1.52			
	333	–2.61			
40	310	–0.41	64.31	32.35	0.99
	318	–0.74			
	333	–1.35			
60	310	–0.41	64.90	48.44	0.94
	318	–0.53			
	333	–1.00			
80	310	–0.05	61.27	36.37	0.91
	318	–0.15			
	333	–0.78			
100	310	–0.20	63.56	37.33	0.97
	318	–0.63			
	333	–1.00			

Table 5
Comparison of maximum adsorption capacities of various adsorbents for dye removal from aqueous solution

Adsorbent	Q_o (mg g^{-1})	Reference
Red mud	4.05	[7]
Coir pith	6.72	[39]
Bagasse fly ash	11.88	[53]
Cashew nut shel	5.18	[54]
Cattail root	38.79	[55]
Kaolin	5.44	[56]
Myrtus communis-based AC	19.2	[57]
Pomegranate-based AC	10	[57]
Orange peel	22.44	[58]
Pine cone	32.65	[59]
Tamarind fruit shell	10.48	[60]
CIFC	43.47	This study

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