

Removal of Chemazol Reactive Red 195 from aqueous solution by dehydrated beet pulp carbon

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ABSTRACT

An agricultural low-cost by-product, dehydrated beet pulp carbon (DBPC) was used as an adsorbent for removal of Chemazol Reactive Red 195 (CRR 195) from aqueous solution. The surface area of DBPC was measured as $9.5 \text{ m}^2 \text{ g}^{-1}$ by using BET method. The results indicated that adsorption was strongly pH-dependent and optimum pH was determined as 1.0. The maximum dye adsorption capacity was obtained as 58.0 mg g^{-1} at the temperature of 50°C at this pH value. The Freundlich and Langmuir adsorption models were used for the mathematical description of the adsorption equilibrium and it was reported that, experimental data fitted very well to Freundlich model. Mass transfer and kinetic models were applied to the experimental data to examine the mechanisms of adsorption and potential rate-controlling steps. It was found that both external mass transfer and intra-particle diffusion played an important role in the adsorption mechanisms of dye and adsorption kinetics followed the pseudo-first-order type kinetic model. The thermodynamic parameters such as, Gibbs free energy changes (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) had been determined. The results show that adsorption of CRR 195 on DBPC is endothermic and spontaneous in nature.

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1. Introduction

Synthetic dyes have been extensively used in many industries such as textile, rubber, plastic, leather tanning, paper production, food technology, photoelectrochemical cells, etc. [1–3]. The discharge of coloured wastes into receiving streams causes serious environmental problems such as affecting photosynthetic activity in aquatic life due to reduced light penetration because of persistent and recalcitrant nature of various dyes [4]. They are toxic to some aquatic organisms and are of serious health risk to human beings [5]. Reactive dyes are the most problematic compared to other forms of dyes and must be removed from wastewater completely. Since many synthetic dyestuffs are resistant to biological degradation due to their complex aromatic molecular structures and colour removals by traditional biological processes are difficult and not complete [3,6,7]. Many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electro-dialysis, membrane separation and oxidation have been used for the treatment of dye-containing effluents. Although these techniques have been shown to be effective, they have limitations such as, excess amount of chemical usage, or accumulation of concentrated sludge, expensive plant requirements or operational costs, lack of effective colour reduction, and sensitivity to a variable

wastewater input [5,8–12]. Adsorption methods have been invariably successful to decolourise textile effluents, but this application is limited by the high cost of adsorbents. Activated carbons are usually produced from high carbon content materials and have a high degree of porosity and an extensive surface area. These materials are effective adsorbents for several organic compounds of concern in water and wastewater treatment [13,14]. Activated carbon is quite expensive and the higher the quality the greater the cost. In the past few years, extensive research has been undertaken to develop alternative and economic adsorbents. Some of the materials used with varying success include: sawdust, rice husk, rice shells, peanut shells, cotton seed shell, myrobalan, rubber seed coat, cashewnut sheath, palm seed coat, palm tree flower, pongam seed coat, cornelian cherry, apricot stone, almond shell, oak wood waste, corn hulls, corn stover and cotton stalks [15–34].

In this study, an agricultural low-cost by-product, Dehydrated beet pulp carbon (DBPC) was used as an adsorbent. Beet pulp is a complex material basically containing lignin and cellulose as the major constituents. Beet pulp carbon obtained from different methods to use as an adsorbent was studied for removing pollutants such as phenol and heavy metals [35,36]. But the studies focusing on dye adsorption on beet pulp carbon are very limited and there is still lack of works on evaluating equilibrium, kinetic and thermodynamic parameters of the process.

The objective of this study was to produce DBPC as an adsorbent for adsorption of Chemazol Red 195 (CRR 195) dye, to characterise it and to investigate the effects of initial dye concentration,

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Nomenclature

C	unadsorbed dye concentration in solution at any time (mg L^{-1})
C_{eq}	unadsorbed dye concentration in solution at equilibrium (mg L^{-1})
C_0	initial dye concentration (mg L^{-1})
d_p	particle diameter (cm)
K_b	adsorption equilibrium constant (L mg^{-1})
K_F	Freundlich constant
k_L	external mass transfer coefficient (cm min^{-1})
K	intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$)
k_1	rate constant of pseudo-first-order sorption (min^{-1})
k_2	rate constant of pseudo-second-order sorption ($\text{g mg}^{-1} \text{min}^{-1}$)
n	Freundlich constant
N	Number of data points
q	adsorbed dye quantity per gram of adsorbent at any time (mg g^{-1})
q_{eq}	adsorbed dye quantity per gram of adsorbent at equilibrium (mg g^{-1})
q_{max}	maximum amount of dye per unit weight of the adsorbent to form a complete monolayer on the surface (mg g^{-1})
R	Universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
R^2	regression correlation coefficient
t	time (min)
T	temperature ($\text{K}, ^\circ\text{C}$)
X	sorbent concentration (g L^{-1})
ΔG°	Gibbs free energy change
ΔH°	enthalpy change of adsorption
ΔS°	entropy change of adsorption
SD	normalized standard deviation
ρ_p	particle density (g mL^{-1})

contact time, temperature and pH. Equilibrium isotherm data were fitted to Langmuir and Freundlich equations and constants of isotherm equations were determined. The mechanisms of chemozole red sorption onto DBPC and potential rate-controlling steps were examined by using external mass transfer and intraparticle diffusion models. Furthermore pseudo-first and second-order kinetic models were also used to analyse adsorption kinetics. Finally, thermodynamic parameters were evaluated using adsorption data.

1.1. Adsorption equilibrium

Equilibrium study provides fundamental information required to evaluate the affinity or capacity of an adsorbent, which is one of the most important criteria in selecting a suitable adsorbent. Meanwhile, equilibrium behavior of an adsorption system is an essential prerequisite during mathematical modeling of the adsorption kinetics. Among the available adsorption equilibrium isotherm models, the most generalized model is a correlative equation proposed by Langmuir [37]. The Langmuir model is valid for monolayer adsorption onto a surface with a finite number of identical sites, which are homogeneously distributed over the adsorbent surface. The well-known expression of the Langmuir model is given as:

$$q_{\text{eq}} = \frac{q_{\text{max}} K_b C_{\text{eq}}}{1 + K_b C_{\text{eq}}} \quad (1)$$

where q_{eq} is the dye adsorbed on carbon at equilibrium, C_{eq} is the equilibrium concentration in the solution, q_{max} is the adsorption capacity and K is the adsorption equilibrium constant related to energy of adsorption.

The Freundlich model is, however, an empirical equation based on adsorption on a heterogeneous surface, suggesting that binding sites are not equivalent and/or independent. Freundlich equation is expressed as [38]:

$$q_{\text{eq}} = K_F C_{\text{eq}}^{1/n} \quad (2)$$

where K_F is an indicator of the adsorption capacity and n is an indicator of the adsorption intensity.

1.2. Adsorption kinetics

In the removal of dyes from wastewater, it is necessary to know the rate of adsorption for process design, operation control and evaluation of adsorbent. Adsorption kinetics of CRR 195 onto DBPC is mainly controlled by three consecutive steps including diffusion processes [4,39]. Adsorbate (dye) transport from the boundary film to the surface of the sorbent (film diffusion), transfer of adsorbate from the surface to the intraparticle active sites (intraparticle diffusion), uptake of adsorbate by the active sites on the surface of the adsorbent. The last step is considered to be an equilibrium reaction and assumed to be rapid while the other steps are the rate determining steps, either singly or in combination.

1.2.1. External mass transfer model

In the first step of adsorption, the film diffusion (external mass transfer) is an important rate-controlling step and boundary model was used in this study (Eq. (3)). According to this model, the change in dye concentration with respect to time is related to the liquid–solid mass transfer coefficient (external mass transfer coefficient) k_L [39,40],

$$\frac{dC}{dt} = -k_L S (C - C_s) \quad (3)$$

where C is the liquid phase solute concentration of dye at a time t , C_s the liquid phase solute concentration at the particle surface; and S the specific surface area for mass transfer. It is assumed that during the initial stages of adsorption, the intraparticle resistance is negligible and the transport is mainly due to film diffusion mechanism. At $t=0$, the surface concentration of dye, C_s , is negligible and $C=C_0$. With these assumptions Eq. (3) can be simplified as;

$$\frac{d(C/C_0)}{dt} = -k_L S \quad (4)$$

Assuming the adsorbent particles are spherical, S is calculated from Eq. (5);

$$S = \frac{6X}{d_p \rho_p} \quad (5)$$

where X is the sorbent concentration in the solution, d_p the average particle diameter and ρ_p is the density of the sorbent. By plotting C/C_0 against t , the value of k_L may be determined from the slope at $t=0$.

1.2.2. Intraparticle mass transfer diffusion model

In the model developed by Weber and Morris, the rate of intraparticle diffusion is a function of $t^{1/2}$ and can be given by the following equation [41,42],

$$q = f \left(\frac{Dt}{r_p^2} \right)^{0.5} = Kt^{0.5} \quad (6)$$

where r_p is the particle radius, D the effective diffusivity of solutes within the particle, and K is the intraparticle diffusion constant.

According to this model, the plot of q versus $t^{0.5}$ should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the only rate-controlling step. Otherwise, some other mechanisms along with intraparticle diffusion are also involved. K -values can be determined by linearizing the curve $q = f(t^{0.5})$.

1.2.3. Pseudo-first-order and pseudo-second-order models

Pseudo-first-order and pseudo-second-order models can be used to test the adsorption process. The pseudo-first-order reaction rate model known as the Lagergren kinetic equation is widely employed [43].

$$\frac{dq}{dt} = k_1(q_{eq} - q) \quad (7)$$

where q is adsorbed dye quantity per gram of sorbent at any time (mg g^{-1}), k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). The integrated form of the differential equation becomes,

$$\log(q_{eq} - q) = \log(q_{eq}) - \frac{k_1}{2.303} t \quad (8)$$

A plot of $\log(q_{eq} - q)$ against of t should give a linear relationship with the slope of $k_1/2.303$ and intercept of $(\log q_{eq})$.

The pseudo-second-order kinetic model is also based on the sorption capacity of the solid phase and on the assumption that the sorption process involves chemisorption mechanism and is expressed as [44];

$$\frac{dq}{dt} = k_2(q_{eq} - q)^2 \quad (9)$$

where k_2 is the rate constant of pseudo-second-order sorption. The integrated form of the differential equation becomes,

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (10)$$

If second-order kinetic equation is applicable, the plot of t/q against t of Eq. (10) should give a linear relationship. The q_{eq} and k_2 can be determined from the slope and intercept of the plot.

The normalized standard deviation for pseudo-first-order and pseudo-second-order models was evaluated using Eq. (11). Where the subscripts 'exp' and 'cal' show the experimental and calculated values respectively and N is the number of data points [45].

$$SD(\%) = 100 \sqrt{\frac{\sum ((q_{t,\text{exp}} - q_{t,\text{cal}})/q_{t,\text{exp}})^2}{N - 1}} \quad (11)$$

1.3. Thermodynamic parameters of adsorption

The thermodynamic parameter of the Gibbs free energy change (ΔG°) reflects the feasibility and spontaneous nature of the process. The free energy change of the adsorption is given by the following equation:

$$\Delta G^\circ = -RT \ln K \quad (12)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K), K_b is the equilibrium constant (The Langmuir constant). The higher negative value of the Gibbs free energy reflects a more energetically favourable adsorption. The equilibrium constant can be used in the Van't Hoff equation to determine the enthalpy (ΔH°) and entropy change of biosorption (ΔS°) as a function of temperature.

$$\ln K_b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

ΔH° and ΔS° can be obtained from the slope and intercept of a plot of $\ln K_b$ versus $1/T$ [46].

2. Materials and methods

2.1. Preparation of dehydrated beet pulp carbon

The beet pulp used in this study is almost a waste material of sugar factory in Elazığ – Turkey. The beet pulp was dried at oven at 105°C for one day. It was grounded and sieved to 30–50 mesh size (0.60–0.30 mm) to remove bigger sizes. Carbon was prepared by mixing one part of beet pulp and two parts concentrated sulfuric acid. The mixture was continuously stirred by a stirrer for about 12 h. At the end of the dehydration process, sufficient distilled water was added to the mixture before filtering by using a water pump. This process was repeated until the final pH of the filtrate was 4.0. The dehydrated carbon rinsed with distilled water was dried for 24 h in oven at 105°C . Finally, dehydrated beet pulp carbon was grounded and screened through different mesh size and stored in a closed bottle to use in adsorption studies later.

The surface area of DBPC measured by using Micromeritics FlowSorb II-2300 was obtained by using N_2 adsorption. To determine adsorption characteristic of DBPC, the iodine number was also measured.

2.2. Chemicals

Chemazol Reactive Red 195 3BS ($\text{MW} = 1136.3 \text{ g mol}^{-1}$) was chosen as the adsorbate, due to its extensive use in the textile industry. It contains one $-\text{N}=\text{N}-$ (azo) bond, vinyl sulfone and monochlorotriazine as reactive groups. Its molecular structure is shown in Fig. 1. It was purchased from Ningbo Mingzhou Chemical Dyestuff Co. Ltd. and used as without further purification.

Stock solution was prepared by dissolving 1.0 g of dye in 1 L of double-distilled water. The test solutions were prepared by diluting of stock solution to the desired concentrations. The range of concentrations of prepared dye solutions changed between 20 and 100 mg L^{-1} . The pH of each solution was adjusted to the required value with diluted or concentrated H_2SO_4 (Merck) and NaOH (Merck) solutions before contacting the sorbent. The preliminary studies showed that the initial pH value did not change considerably during the experimental period.

2.3. Adsorption studies

This method involved agitating (150 rpm) Erlenmeyer flasks of 0.25 L containing 0.15 g DBPC 0.15 L of CRR 195 dye solutions at the desired concentration, temperature and pH. Samples of 5 mL were taken from mixture during stirring at pre-determined time intervals for determining the residual colour concentration in the medium. Before analysis, samples were centrifuged (Nüve CN090) at 5000 rpm for 5 min and supernatant liquid was analysed for the remaining colour. All the experiments were carried out in duplicates and average values were used for further calculations.

2.4. Analysis

The concentration of unadsorbed CRR 195 in the adsorption medium was measured colorimetrically (Jenway 6105 UV/vis. Spectrophotometer). The absorbance of the colour was read at 540 nm, where the maximum absorption peak existed.

The BET surface area was determined from nitrogen adsorption isotherms using a Micromeritics FlowSorb II-2300 Surface Area Analyzer. To determine adsorption characteristic of DBPC, the iodine number (IN) of carbon was determined by shaking 0.5 g of each sample with 100 cm^3 aqueous solution of iodine ($2.7 \text{ g I}_2 \text{ dm}^{-3}$) at 25°C . The gram amount of iodine adsorbed per

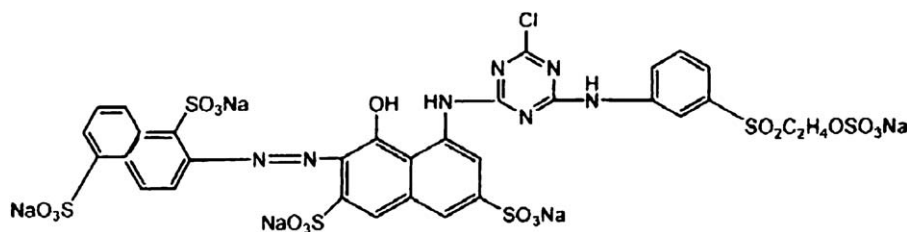


Fig. 1. Molecular structure of CRR 195.

gram carbon was taken as iodine number. The infrared spectrum of DBPC was obtained with a Mattson 1000 FTIR spectromete.

3. Results and discussion

Surface area and iodine number are important characteristics, capable of affecting the quality and utility of adsorbents. For this reason it is important to determine and control them accurately. The BET surface area of the DBPC was determined as $9.5 \text{ m}^2 \text{ g}^{-1}$. Other properties of the DBPC were measured as iodine number $270 \text{ mg I}_2 \text{ g}^{-1}$ and bulk density 0.576 g cm^{-3} .

Adsorption data for the uptake of CRR 195 onto DBPC was investigated at various initial concentration, temperature and pH. The results are given as the units of adsorbed CRR 195 quantity per gram of adsorbent (adsorption capacity) at any time (q) and at equilibrium (q_{eq}), unadsorbed CRR 195 concentration in solution at any time (C) and at equilibrium (C_{eq}). Adsorption yield is given as: $[\text{Ads.}\% = 100 \times (C_0 - C_{\text{eq}})/C_{\text{eq}}]$. Adsorption capacity is given as: $[q = (C_0 - C)/X]$.

3.1. Effect of contact time

Fig. 2 shows the adsorption kinetics of CRR 195 at 25, 40 and 50°C by plotting the dye uptake capacity, versus time. Adsorption studies were carried out for 10 h and it was observed that, the adsorption capacity increased with increasing contact time and temperature and a larger amount of dye was removed in the first 120 min of contact time. Equilibrium was established in 180 min at the end of a rapid adsorption for all the temperatures studied. After an equilibrium time of 200 min, no more CRR 195 was adsorbed.

3.2. Effect of pH on adsorption

An important influencing factor for dye adsorption has been referred to pH in most related studies published in the litera-

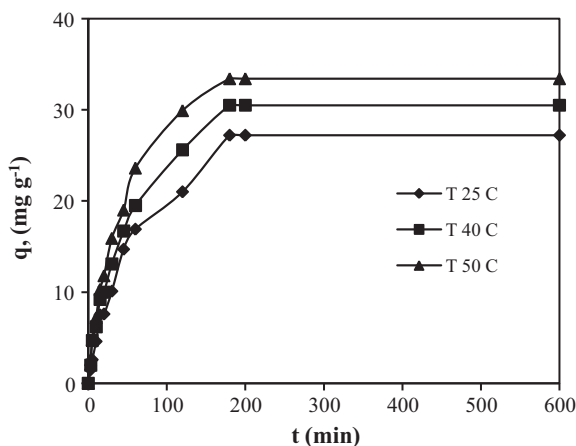


Fig. 2. The adsorption curves of CRR 195 ($C_0 = 40 \text{ mg L}^{-1}$, pH 1.0, $X = 1.0 \text{ g L}^{-1}$, agitation rate = 150 rpm).

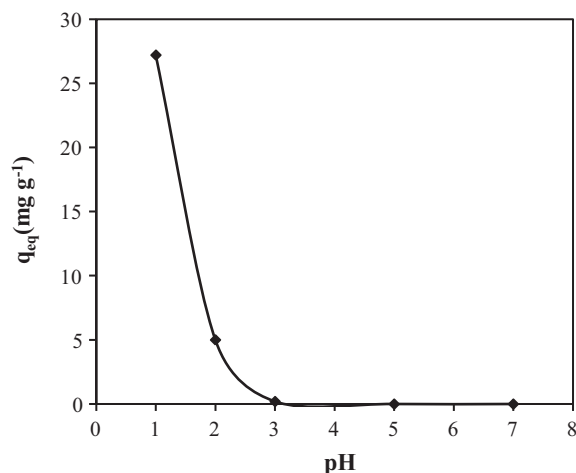


Fig. 3. Effect of pH on the CRR 195 adsorption ($C_0 = 40 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$, $X = 1.0 \text{ g L}^{-1}$, agitation rate = 150 rpm).

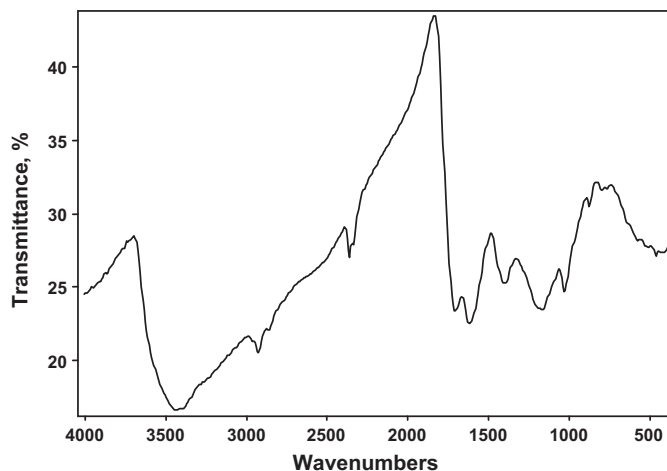


Fig. 4. IR spectra of the DBPC.

ture. To find a suitable pH for the effective adsorption of CRR 195 dye by DBPC, experiments were performed over a pH range of 1.0–7.0. The variation of equilibrium dye uptake with initial pH was given in Fig. 3. The maximum equilibrium uptake value was found as 58.0 mg g^{-1} at pH 1.0 and the adsorption of dye decreased significantly with further increase in pH. The other adsorption experiments were performed at pH 1.0. According to the earlier works stated by Coughlin and Ezra [47], the oxidized carbon were mainly carbonyl and hydroxyl ones, and a very small quantity of carbonyl groups. Fig. 4 shows, the IR spectrum of DBPC. As seen from the figure, DBPC contains several functional groups such as hydroxyl peak at 3408 cm^{-1} , carbonyl peak at 2925 cm^{-1} and asymmetric carboxylate peak at 1630 cm^{-1} . Since the dye species carry negative charge due to sulfonate groups, electrostatic attractions

Table 1

The equilibrium uptake capacities and adsorption yields obtained at different initial concentrations and temperatures.

C_0 (mg L ⁻¹)	25 °C		40 °C		50 °C	
	q_{eq} (mg g ⁻¹)	Adsorption (%)	q_{eq} (mg g ⁻¹)	Adsorption (%)	q_{eq} (mg g ⁻¹)	Adsorption (%)
20	16.4	82.0	18.0	90.0	18.8	94.0
40	27.2	68.0	30.5	76.3	33.4	83.5
75	36.0	48.0	41.0	54.7	47.0	62.7
100	41.0	41.0	51.1	51.1	58.0	58.0

are expected to have a considerable contribution to the overall interactions. Furthermore, solution pH affects both aqueous chemistry and surface binding sites of the adsorbents. Depending on pH, functional groups of the adsorbent may change their valences. It is expected that at pH 1.0, most of the potential fixation sites on DBPC are protonated and the surface of sorbents are surrounded by hydronium ions. Reactive dyes are known to ionize to a high degree in aqueous solutions to form coloured anions due to the sulfonate group(s) in their structures. Sulfonate ($-SO_3^-$) groups of CRR 195 dye are easily dissociated and have negative charges in the aquatic environment. The higher uptakes obtained at very acidic pH could be attributed to the electrostatic interactions between the positively charged sorbent and the negatively charged dye anions. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion.

3.3. Effect of initial CRR 195 concentration on temperature depended adsorption

Effect of temperature on the adsorption of CRR 195 on DBPC was investigated in the temperature range of 25–50 °C at varying initial dye concentrations. The results obtained with 20–100 mg L⁻¹ initial dye concentrations are presented in Table 1. It was indicated that the removal of dye increased with increasing temperature up to 58.0 mg g⁻¹ at 50 °C. The enhancement in adsorption with temperature may be attributed to increase in the number of active surface sites available for adsorption on adsorbent, increase in the porosity and in the total pore volume of the adsorbent. The enhancement in adsorption could be also due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. This may also be a result of an increase in the mobility of the dye molecule with an increase in their kinetic energy, and the enhanced rate of intraparticle diffusion of sorbate with the rise of temperature.

It is clear that the sorption of CRR 195 on DBPC is an endothermic process and may involve not only physical but also chemical sorption.

Table 1 also shows the effect of initial dye concentration on the sorption capacity of DBPC. As a rule, increasing the initial dye concentration results in an increase in the adsorption capacity because the initial dye concentration provides a driving force to overcome mass transfer resistances between the adsorbent and adsorption medium. So higher adsorption capacities were obtained at higher initial concentrations at all temperatures studied. The adsorption yields determined at different initial dye concentrations were also compared in Table 1. Increasing the dye concentration generally caused a decrease in the adsorption yield and the maximum dye adsorption yield determined as 94.0% at an initial concentration of 20 mg L⁻¹ at 50 °C. In the case of lower concentrations, the ratio of dye to the available sorption sites was low and higher biosorption yields were obtained. At higher concentrations, the available sites

of adsorption became fewer and the saturation of the sorption sites was observed. So adsorption yields decreased.

The comparison of adsorption capacity of DBPC used in this study (58.0 mg g⁻¹ for 100 mg L⁻¹ initial CRR 195 concentration at 50 °C, the BET surface area and as iodine number are 9.5 m² g⁻¹ and 270 mg I₂ g⁻¹, respectively) with those obtained in the literature shows that DBPC is effective for this purpose. Gupta et al. [48] studied on removal of indigocarmine dye from industrial effluents by deoiled mustard and charcoal. The adsorption experiments were carried out at 30 °C, pH 3.0 for charcoal and pH 8.0 for deoiled mustard, and adsorbate concentration 2×10^{-4} mol L⁻¹. Amounts of adsorbate were found as approximately 0.33×10^{-4} mol L⁻¹ for 0.40 g L⁻¹ of charcoal and 0.25×10^{-4} mol L⁻¹ for 7.5 g L⁻¹ of deoiled mustard. Jain et al. [49] removed hazardous dye Naphthol Yellow S from wastewater using activated carbon and activated de-oiled mustard. The BET surface area of activated carbon and activated de-oiled mustard was 929.7 ± 2.1 and 326.5 ± 3.4 m² g⁻¹, respectively. Amounts of adsorbate were determined as approximately 8.0×10^{-5} mol L⁻¹ and 7.0×10^{-5} mol L⁻¹ for 0.5 g L⁻¹ activated carbon and 4 g L⁻¹ activated de-oiled mustard, respectively. Mittal et al. [50] investigated adsorption of Chrysoidine Y on bottom ash and de-oiled soya. The dye sorption capacities of bottom ash (BET surface area = 870.5 cm² g⁻¹) and de-oiled soya (BET surface area = 728.6 cm² g⁻¹) were determined as 3.61×10^{-5} mol g⁻¹ and 1.92×10^{-5} mol g⁻¹ at 30 °C, respectively. Gupta et al. [51] used bottom ash and de-oiled soya for adsorption of carmoisine, the maximum uptake of dye was found to be 1.962×10^{-5} mol g⁻¹ for bottom ash and 3.13×10^{-5} mol g⁻¹ for de-oiled soya at 323 K. Özer and Dursun [52] presented the methylene blue adsorption capacity of dehydrated wheat bran (BET surface area = 9.5 m² g⁻¹) as 99.84 mg g⁻¹ for initial methylene blue concentration of 200 mg L⁻¹ at 45 °C. Acemioglu [53] investigated adsorption of methylene blue onto perlite. They found the equilibrium uptake between 28 and 94 mg g⁻¹ for various initial dye concentrations. Ferrero [54] studied with hazelnut shell for removal of Acid blue 25. The maximum uptake of dye was found to be 60.2 mg g⁻¹ at the pH value 4.5. Chen et al. [55] determined basic red 22 adsorption capacity of bagasse pith raw as 75 mg g⁻¹. Mane and Babu [56] studied on adsorptive characteristics of brilliant green dye from aqueous solution onto NaOH treated sawdust (BET surface area = 0.3742 m² g⁻¹). The adsorption capacities of sawdust were obtained as 58.4795, 55.8659 and 52.6315 mg g⁻¹ at 288, 303 and 318 K, respectively.

3.4. Determination of equilibrium parameters

Equilibrium data, provide basic requirements for the design of adsorption systems such as; interaction of adsorbates with adsorbent, information about the capacity of the adsorbent. The most widely used isotherms equation for modeling of the adsorption data are the Langmuir and Freundlich equations. Initial dye concentrations were varied from 20 to 100 mg L⁻¹ while the adsorbent concentration was kept constant (1 g L⁻¹) at 25, 40 and 50 °C. The linearised isotherms plots are presented in Figs. 5 and 6 for the Langmuir and Freundlich equations, respectively. Table 2 shows the values of adsorption model constants, which express the surface properties, adsorption mechanisms and capacity or affinity of

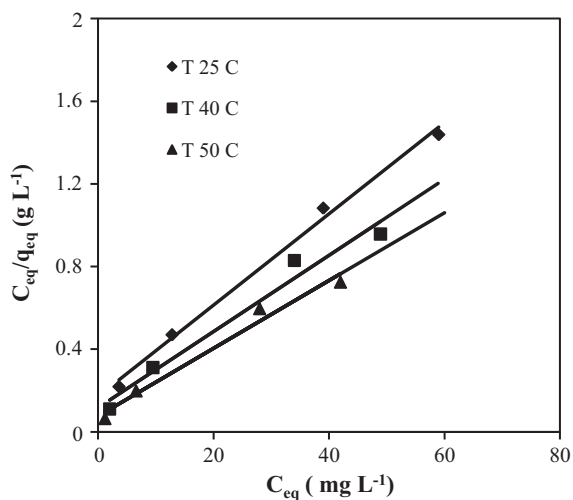


Fig. 5. The linearized Langmuir adsorption isotherm of CRR 195.

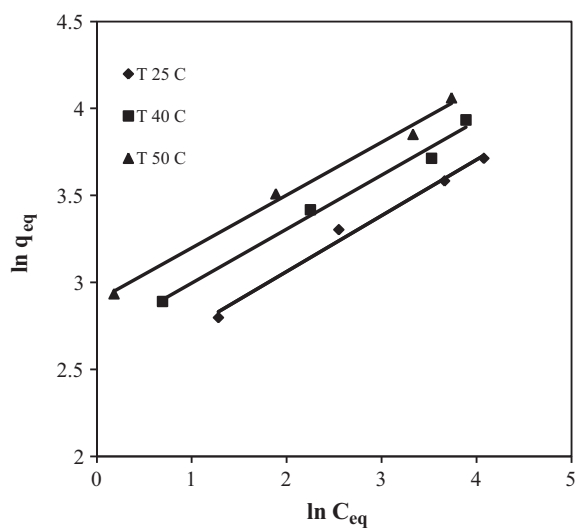


Fig. 6. The linearized Freundlich adsorption isotherm of CRR 195.

Table 2
Isotherms constants for CRR 195 adsorbed on DBPC.

T (°C)	Langmuir model			Freundlich model		
	q_{\max}	K_b	R^2	K_F	n	R^2
25	45.24	0.1286	0.9946	11.22	3.11	0.9884
40	54.35	0.1567	0.9730	14.66	3.22	0.9880
50	60.98	0.2152	0.9781	18.05	3.29	0.9917

the sorbent. K_F , one of the Freundlich constants has been used as a relative measure of adsorption capacity. The values of K_F increased with the rise in temperature and the highest K_F values were determined as 18.05 at 50 °C. The n , the other Freundlich constant, is an empirical parameter that varies with the degree of heterogeneity indicating the degree of non-linearity between dye uptake capacity of adsorbent and unadsorbed dye concentration. Since the n values obtained from the isotherms are higher than 1.0, CRR 195 are favourably adsorbed by the DBPC at all temperatures studied. Both the q_{\max} and K -values determined from Langmuir equation increased from 45.24 to 60.98 and from 0.1286 to 0.2152 with increasing temperature from 25 °C to 50 °C respectively. The maximum capacity, q_{\max} defines the monolayer saturation at equilibrium or the total capacity of the adsorbent for dye. The other

Langmuir constant, K indicates the affinity for the binding of CRR 195. The higher value of K found at 50 °C showed strong bonding of CRR 195 to the DBPC at this temperature. As seen from Table 2 although correlation coefficients of two equations are considerably well obtained, the Freundlich model exhibited best fit to the adsorption data than the other model.

3.5. Kinetic parameters of adsorption

Batch adsorption studies were carried out to identify the potential rate controlling steps for design and evaluation of adsorbent. External film mass transfer, intraparticle diffusion and pseudo-first and second-order kinetic models were used to test the dynamics of sorption process and attempts were made to calculate the coefficients of these models.

External mass transfer is characterized by the initial rate of solute diffusion for the system studied. The plots of C/C_0 versus t obtained at all initial dye concentrations and at 25, 40 and 50 °C (data not shown) indicated that the concentration of dye falls very fast during the initial uptake before intraparticle diffusion could begin to control the adsorption kinetics for all cases. The external mass transfer coefficients were determined from the slopes as $t \rightarrow 0$ and presented in Table 3. The results showed that the increase in initial dye concentration resulted in a decrease in the external mass transfer coefficient and external mass transfer. It was also indicated that the values of external mass transfer coefficient increased with increasing temperature. This may be a result of an increase in the mobility of the dye molecule with an increase in their kinetic energy, and the enhanced rate of external mass transfer of sorbate with the rise of temperature. It is clear that, as expected, external mass transfer cannot be neglected, although this resistance is only significant for the initial period of adsorption time.

The plots of Q against the $t^{0.5}$ at all initial dye concentrations and at 25, 40 and 50 °C temperatures (data not shown) revealed that all the plots have the same general feature presenting multilinearity, indicating that a few steps took place. The first, sharper portion obtained in very beginning period which extent is related to initial dye concentration and temperature, is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second linear portion describes the gradual layer adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage for which the intraparticle diffusion started to slow down due to the low dye concentration left in the solution. The linear plots of second portion at each concentration and temperature did not pass through the origin, this is indicative of some degree of boundary layer control and this shows further that the intraparticle diffusion is not only rate-controlling step. The values of K evaluated from these linear parts of plots are also tabulated in Table 3. As seen from the table, K values increased with increasing initial dye concentration and temperature.

The plots of linearised form of the pseudo-first-order and pseudo-second-order equations are shown in Figs. 7 and 8 respectively. The values of k_1 , k_2 , q_{eq} and correlation coefficients are compared in Table 4. As seen from the table, the correlation coefficients for the first-order model obtained were closed to the second-order kinetic model's correlation coefficients and all of the correlation coefficients were high. But the theoretical q_{eq} values agreed very well with the experimental q_{eq} values in the case of pseudo-first-order kinetics, while pseudo-second-order model did not give reasonable values. Furthermore, in order to quantitatively compare the applicability of each model, a normalized standard deviation was evaluated using Eq. (11) and the normalized standard deviation value for pseudo-first-order model ($SD=8,49$) was found to be lower than the pseudo-second-order kinetic model's ($SD=38,56$). These suggest that the sorption process may be best

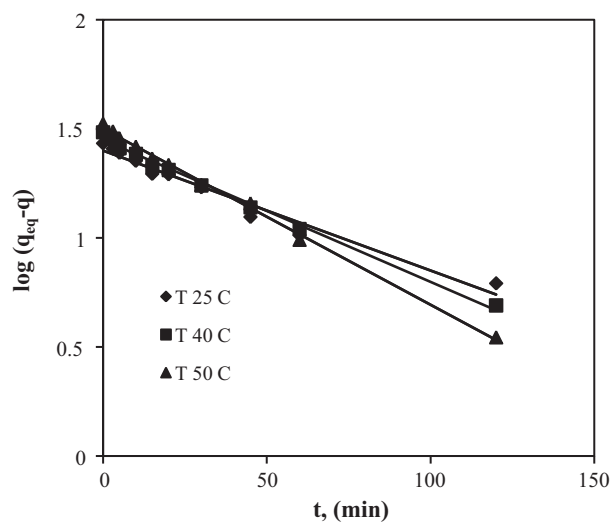
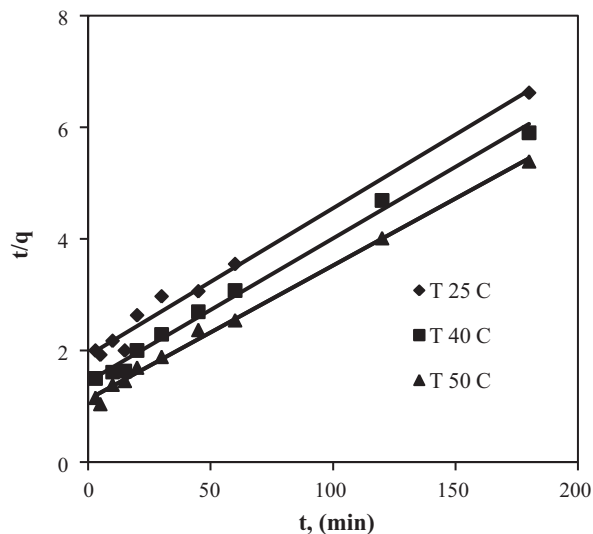
Table 3Effect of initial CRR 195 concentration and temperature on the external mass transfer coefficients (k_L) and intraparticle diffusion rate constants (K).

C_0 (mg L ⁻¹)	25 (°C)		40 (°C)		50 (°C)	
	k_L (cm min ⁻¹)	K (mg g ⁻¹ min ^{-0.5})	k_L (cm min ⁻¹)	K (mg g ⁻¹ min ^{-0.5})	k_L (cm min ⁻¹)	K (mg g ⁻¹ min ^{-0.5})
20	0.094771	1.497	0.107843	1.623	0.125817	1.849
40	0.040850	2.642	0.076797	2.904	0.078431	3.194
75	0.033987	3.263	0.056536	3.561	0.071569	4.054
100	0.029902	3.421	0.055556	4.569	0.059804	6.687

Table 4

Change of the pseudo-first- and second-order reaction rate constants with temperature.

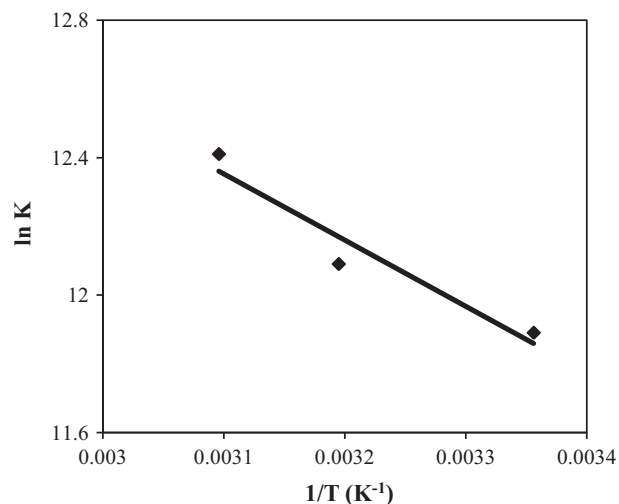
T (°C)	$q_{eq,exp}$ (mg g ⁻¹)	First-order kinetic model			Second-order kinetic model		
		k_1 (min ⁻¹)	$q_{eq,cal}$ (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{eq,cal}$ (mg g ⁻¹)	R^2
25	27.20	0.01267	25.14	0.968	0.000364	37.88	0.987
40	30.50	0.01497	28.14	0.992	0.000454	39.06	0.993
50	33.40	0.01865	31.67	0.997	0.000513	41.67	0.995

**Fig. 7.** Pseudo-first-order adsorption kinetics of CRR 195 at different temperatures.**Fig. 8.** Pseudo-second-order adsorption kinetics of CRR 195 at different temperatures.

described by the pseudo-first-order with external mass transfer and intraparticle diffusion as one of the rate determining steps.

Table 5 ΔG° values for adsorption of CRR 195 at different temperatures.

T (°C)	K_b (L mg ⁻¹)	$-\Delta G^\circ$ (kJ mol ⁻¹)
25	0.1286	29.46
40	0.1567	31.46
50	0.2152	33.31

**Fig. 9.** $\ln K_b$ vs. $1/T$ plot.

3.6. Thermodynamic parameters of adsorption

The Gibbs free energy changes for the adsorption process were calculated by using the equilibrium constants obtained from Langmuir model and tabulated in Table 5. As it is seen from the table all the Gibbs free energy change values are negative; a negative value of ΔG° indicates the feasibility of the process and spontaneous nature of the adsorption. The standard enthalpy change of adsorption determined from the $\ln K_b$ versus $1/T$ plot (Fig. 9) was 16.019 kJ mol⁻¹. The positive value of ΔH° suggests the endothermic nature of biosorption. The entropy changes of the adsorption at 25, 40 and 50 °C were determined as 0.099, 0.152 and 0.153 kJ mol⁻¹ K⁻¹, respectively. The positive value of ΔS° confirms the increased randomness at the solid–solution interface during adsorption.

4. Conclusion

The aim of this work was to explore the possible use of, dehydrated carbon prepared from beet pulp, which is agricultural low-cost by-product available in large quantities in Turkey as sorbents for the removal of textile dye Chemazol Reactive Red 195 from aqueous solutions. The results indicated that adsorption was strongly pH-dependent and optimum pH was determined as 1.0. The dye sorption occurred rapidly initially and then proceeded gradually to equilibrium and equilibrium was established in 180 min. The Langmuir and Freundlich adsorption models were used to express the adsorption phenomenon. It was indicated that, the Freundlich model provided a better fit than the other at all the temperatures studied. External mass transfer, intraparticle diffusion models were applied to examine the mechanisms of sorption and potential rate-controlling steps. The sorption process was found to be controlled by both film and pore diffusion with film diffusion at the earlier stages followed by pore diffusion at the later stages. The pseudo-first-order and pseudo-second-order kinetic models were also used to test adsorption kinetics. It was shown that the adsorption of CRR 195 dye on to DBPC could be best fitted to the pseudo-first-order model. These kinetic parameters obtained can be used for reactor design. Thermodynamic parameters such as change in free energy, enthalpy, and entropy were also determined. The results show that adsorption of CRR 195 on DBPC is an endothermic and spontaneous in nature.

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