Removal of disperse dye from aqueous solution by novel adsorbent prepared from biomass plant material

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ABSTRACT

The adsorption of Disperse Orange 25 (3-[*N*-ethyl-4-(4-nitrophenylazo) phenylamino] propionitrile) onto activated carbon was investigated in a batch system with respect to contact time, carbon dosage, pH and temperature from aqueous solutions. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. The Langmuir isotherm model agrees with the experimental data well. Maximum adsorption capacity (q_{max}) of Disperse Orange 25 onto adsorbent was 118.93 mg g^{-1} at 20 °C. The first-order, pseudo-second-order kinetic models and the intraparticle diffusion model were used to describe the kinetic data and the rate constants were evaluated as well. The experimental data fitted very well to pseudo-second-order kinetic model. The results show that activated carbon prepared from *Euphorbia rigida* by sulfuric acid chemical activation could be employed as low-cost material to compare with commercial activated carbon for the removal of disperse dyes from effluents.

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1. Introduction

Disperse dyes are widely used in variety of industries, such as textiles, paper and leather. Disperse dyes are non-ionic aromatic compounds, scarcely soluble in water but soluble in organic solvent. The majority of them are azo and anthraquinone dyes. These dyes can be applied to synthetic fibers such as polyester, nylon, acetate, cellulose and acrylic [1]. Textile industries effluent contains many dyes which are containing carcinogen and mutagen chemicals such as benzidine, metals, etc. and causes serious environmental problems. Dyes are visible even at low concentrations and are difficult to biodegrade in the environment due to their resistance to light, heat, chemical and water [2]. In this manner, these kinds of pollutants must be treated prior to their discharge into the receiving water bodies. The conventional treatments of dyed wastewater include chemical coagulation, biological and electrochemical processes, ozonation and adsorption [3–8]. Coagulation is the process in which destabilization of colloidal and suspended particles occurs and flocculation follows coagulation by agglomeration of these particles. Destabilization is usually brought about by changing the solution pH value or by adding chemicals. But it still has many problems such as chemical waste production. Ozone oxidation is efficient decolorization method, but it has high equipment and operating cost. Because electrochemical processes are, costly in some cases; especially in dilute wastewater, new methods and materials have been proposed [6,9].

Adsorption onto activated carbon has been proven to be an effective process for dye removal, but it is an expensive process. This has largely been associated with the cost of producing activated carbon, and the lack of suitable and inexpensive regeneration procedures for these adsorbents. The activation method to be proposed is important for the cost of producing activated carbons. In this respect, these have led many researchers to use low-cost plant and wood-based materials for activated carbon production. Numerous low-cost plants, agricultural and/or wood-based materials such as pistachio shells [10,11], palm kernel shell [12], date piths [13,14], rice bran [15], coir pith [16,17], rice husk [18–19] and mango seed kernel powder [20], have been used for the production of activated carbon for the removal of the textile dye effluents.

The aim of this study was to evaluate the ability of using activated carbon prepared from *Euphorbia rigida* by sulfuric acid chemical activation for the adsorption of disperse dye from aqueous solutions. The effects of initial dye concentration, contact time, pH and temperature on the adsorption of Disperse Orange 25 (DO25) dye onto activated carbon prepared from *E. rigida*, which is a plant-based material and a biomass source, were investigated. The

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Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. The first-order, pseudo-second-order kinetic models and the intraparticle diffusion model were used to describe the kinetic data and the rate constants were evaluated as well.

2. Materials and methods

2.1. Adsorbent and adsorbate

E. rigida, which is a member of the Euphorbiaceae family plant, mostly grows in arid land regions in Turkey. This family of plants included around 2000 species, ranging from small herbs to large trees. Euphorbiaceae family plants can produce milky latex, which yields wide range of chemicals of interest to various industries but it does not use for the food production [21–23].

E. rigida was used in this study as a source of activated carbon, collected from nearby Afyon, Turkey. It was dried at room temperature and carbonized with 50% sulfuric acid as a chemical reagent added during the chemical activation process helps produce more effective adsorbent. The carbonization was completed by heating rate of $10\,°C\,min^{-1}$ to the final carbonization temperature of $850\,°C$ for 30 min. After cooling, the activated carbon was repeatedly washed with deionized water and dried at $105\,°C$. The carbonized material was sieved to $125–250\,\mu m$ size and used for adsorption experiments [24]. Activated carbon was characterized with respect to the surface area which was examined at 77 K by means of a standard BET procedure N_2 adsorption (Quantachrome Inst., Nova 2200e Surface Area Analyzer). BET equation was used to calculate the specific surface area. Before the measurements activated carbon was degassed at $300\,°C$ for 3 h. The surface area of activated carbon is $741.21\,m^2\,g^{-1}$.

Disperse dye selected for use in this study was DO25 and used as received without further purification. The chemical structure of DO25 is illustrated in Fig. 1. A stock solution of dye was prepared by dissolving an accurate quantity of dye in deionized water and acetone (40/60, v/v). Other concentrations prepared from stock solution by dilution varied between 50 and $125\,mg\,dm^{-3}$ and the pH of the working solutions was adjusted to desired values with 0.1 M HCl or 0.1 M NaOH. Fresh dilutions were used for each experiment.

In investigation of dyeing process, the dye concentration is calculated according to the Beer Lambert's law and is measured by spectrophotometer. In the analysis of waste water containing disperse dyes, the presence of water cannot be eliminated, and therefore the choice of a suitable organic solvent to be added, and the determination of an optimum mixture aqueous dispersion/organic solvent is of great importance in the visible spectroscopy of disperse dyes [25]. In this study, aqueous/organic solvent ratio of 40/60 (v/v) was used.

2.2. Equilibrium studies

The batch adsorption studies were performed using a mechanical magnetic stirrer at 200 rpm in a 100-mL Erlenmeyer sealed
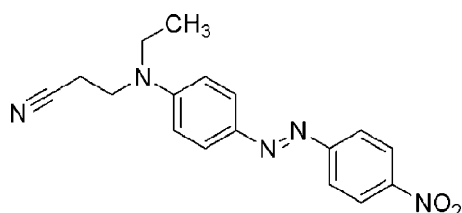
with parafilm to avoid evaporation. The effect of pH on the amount of dye adsorbed onto activated carbon from *E. rigida* by H_2SO_4 activation was studied in the pH range from 4 to 9 with a fixed carbon concentration (0.1 g in 50 mL of $100\,mg\,dm^{-3}$ of dye solution) agitated for 150 min at $20\,°C$. The pH was carefully adjusted by adding a small amount of dilute HCl or NaOH solution using a pH meter. The optimum pH was then determined as 7 and used throughout all adsorption experiments, which were conducted at various time intervals to determine the adsorption equilibrium time and the maximum removal of disperse dye. The effect of adsorbent concentration was studied by using adsorbent ranging from 0.2 to $2\,g\,dm^{-3}$. For isotherm studies, accurately weighted amount of (0.06 g) activated carbon was continuously stirred at 200 rpm with 50 mL of ($50–125\,mg\,dm^{-3}$) dye solutions. The adsorption of DO25 onto activated carbon from *E. rigida* by H_2SO_4 activation was also evaluated at constant temperatures of $10–20\,°C$ for the adsorption isotherms. After the desired contact time, solutions were centrifuged for 5 min at 3500 rpm and the dye concentration was measured by spectrophotometer (Shimadzu UV-2101PC) at the λ_{max} value, which is 475 nm for DO25. The amounts of disperse dye adsorbed were calculated from the final solution concentrations and the initial concentration of aqueous solution.

3. Results and discussion

3.1. Effect of pH

The pH of the solution was an important controlling parameter in the adsorption process. Fig. 2 indicates the effect of pH on the removal of the DO25 onto activated carbon from *E. rigida* by H_2SO_4 activation from aqueous solution. It was observed that the adsorption of DO25 is unaffected by changing solution pH and remained nearly constant over the initial pH ranges of 4–9. The percentage adsorption of DO25 was not significantly changed when the initial pH was increased from 4 to 9. Thus pH 7 was selected as the optimum pH value for all further experiments due to the advantage of neutral pH value.

The effect of the solution pH is extremely important when the adsorbing species is capable of ionizing in response to the prevailing pH. It is well known that substances adsorb poorly when they are ionized. When the adsorbing species is not ionized, no such electrical repulsion exists, and thus the packing density on the surface can be higher. Of course, there have been many studies, particularly in the chemistry, chemical and environmental engineering literature,
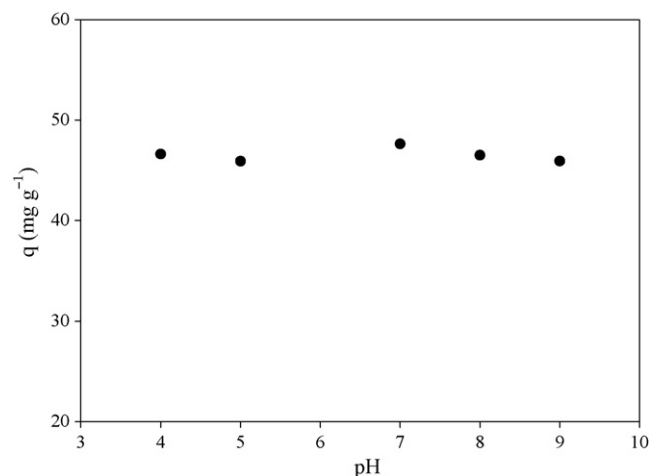

Fig. 1. The chemical structure of C.I. Disperse Orange 25 (DO25).

Fig. 2. Effect of pH for the adsorption of DO25 onto activated carbon from *E. rigida* at $20\,°C$.
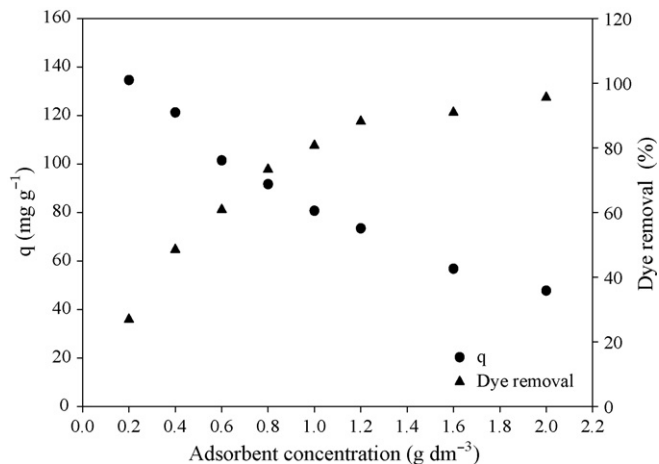
Fig. 3. Effect of adsorbent concentration for the adsorption of DO25 onto activated carbon from *E. rigida* at 20 °C.
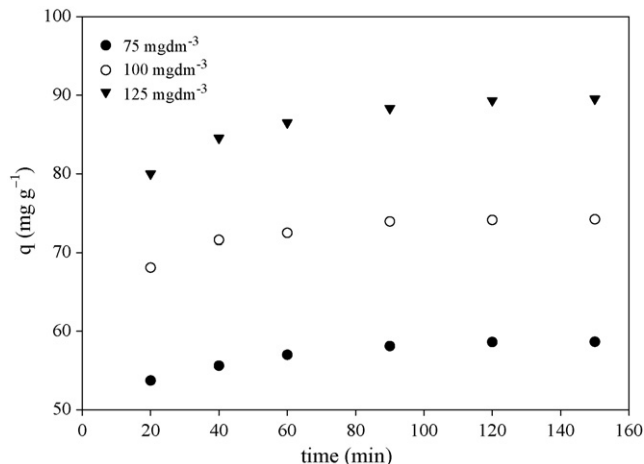

Fig. 4. Effect of contact time for the adsorption of DO25 onto activated carbon from *E. rigida* at 20 °C and various initial dye concentrations.

on the effect of pH on the adsorption of the organic substances to activated carbon. As the pH of the system increases, the surface of the adsorbent tends to become negatively charged, which does not favour the adsorption of disperse dye due to electrostatic repulsion. At the same time, the presence of excess OH⁻ ions in alkaline pH will compete with the dye anions for the adsorption sites. In addition, disperse dyes are hydrophobic. As the solubility of disperse dyes in aqueous solution is low, they have a tendency to accumulate at the surface of adsorbents [26]. It was found that the adsorption of DO25 onto activated carbon remained approximately constant in the pH range of 4–9. Isa et al. [8] also reported a similar trend for the adsorption of disperse blue and disperse red onto palm ash surface and the percent removal of disperse dyes remained approximately constant in the pH range of 5–10. Ramakrishna and Viraraghavan [26] also reported a similar observation for the adsorption of disperse red 1 dye onto slag in pH range of 5–11.

3.2. Effect of adsorbent concentration

The results of the experiments with varying adsorbent concentrations are presented in Fig. 3. It was observed that the amount of dye adsorbed decreased from 134.53 to 47.76 mg g⁻¹ with increasing in the adsorbent concentration from 0.2 to 2.0 g dm⁻³. However the percentage of dye removal increased from 26.90 to 95.52% in the same adsorbent concentration range. Increase in the amount of adsorbed dye with adsorbent dosage can be attributed to increased adsorbent surface area of mesopores and the availability of more adsorption site, but the adsorption capacity decreased with an increase in the adsorbent dosage. This suggests that adsorbed species may either block the access to the internal pores or cause particles to aggregate and thereby resulting in unavailability of active sites for adsorption.

It is possible that the amount adsorbable dye per unit adsorbent mass increases by decreasing the adsorbent dose and it, therefore, results in the increase of the amount of adsorbed dye. Higher dye concentration resulted in higher driving force of the concentration gradient. This driving force accelerated the diffusion of dyes from the solution into the adsorbent. A similar trend was reported for the adsorption of dyes such as Congo Red onto activated carbon and bagasse fly ash [27], metal complex dye onto pine sawdust [28], Congo Red onto Neem leaf powder [29] and Basic Black dye onto calcium alginate [30]. The optimum amount of activated carbon from *E. rigida* for further adsorption experiments

was selected as 1.2 g dm⁻³. Because of the removal efficiency at 2.0 g dm⁻³ of adsorbent concentration was not much higher than that at 1.2 g dm⁻³.

3.3. Effect of contact time and initial dye concentration

The adsorption capacity of DO25 removed by activated carbon from *E. rigida* versus contact time for different initial dye concentration is illustrated in Fig. 4. The removal of DO25 onto activated carbon from *E. rigida* was rapid initially and then slows down gradually until it attained an equilibrium beyond which there was no significant increase in the removal at all dye concentrations. It can be seen that the adsorbed amount of DO25 increased with contact time up to 90 min, at that point a maximum removal was attained.

An increase in the initial dye concentration from 75 to 125 mg dm⁻³ lead to an increase in the amount of dye from 58.66 to 89.54 mg g⁻¹ adsorbed onto activated carbon.

3.4. Effect of temperature

The adsorption capacity of DO25 as a function of temperature at optimum pH values, adsorbent concentration of 1.2 g dm⁻³ and initial dye concentrations of 125 mg dm⁻³ are given in Fig. 5. The
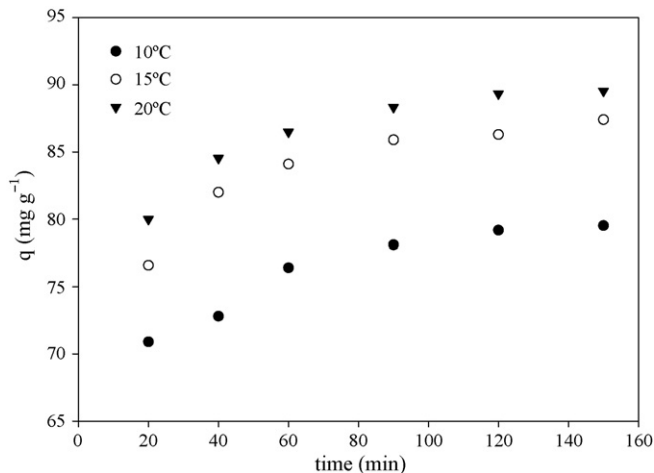

Fig. 5. Effect of temperature for the adsorption of DO25 onto activated carbon from *E. rigida*.

equilibrium adsorption capacity of DO25 onto activated carbon from *E. rigida* increased with increasing temperature from 10 to 20 °C which indicates that the adsorption of DO25 onto activated carbon from *E. rigida* surface was favoured at higher temperatures and it is controlled by an endothermic process.

3.5. Adsorption isotherms

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. In this manner, the Langmuir [31], the Freundlich [32], and the D–R [33], isotherm equations were used to interpret the experimental data.

Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface, i.e., the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption and that the adsorbent is saturated after one layer of adsorbate molecules forms on to surface [34]. The linearized form of the Langmuir adsorption isotherm equation is

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (1)$$

The Langmuir constants, which are q_m and K_L values, can be calculated from the plot C_e/q_e versus C_e. Fig. 6 shows the Langmuir adsorption isotherms of the DO25 onto activated carbon from *E. rigida*. The maximum adsorption capacity was determined as 118.93 mg g^{-1} at 20 °C. All of the isotherm model parameters for the DO25 onto activated carbon from *E. rigida* are tabulated in Table 1.

The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor of equilibrium parameter, which is defined by [35,36]:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (2)$$

where K_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution.

The value of R_L calculated from Eq. (2) is incorporated in Table 1. R_L values between 0 and 1 at different concentrations indicate
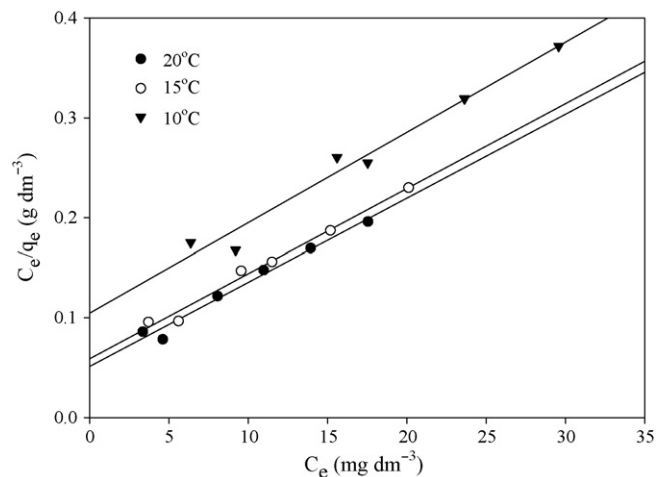

Fig. 6. Langmuir plots for the adsorption of DO25 onto activated carbon from *E. rigida*.

favourable adsorption of dye onto activated carbon. Further, the R_L values for this study are between 0.085 and 0.046, therefore, the adsorption is favourable [36].

The adsorption capacity of activated carbon from *E. rigida* from Langmuir isotherm equation for disperse dye is comparable and was found to be the higher than that of many corresponding adsorbent reported in the literature (Table 2) [5,8,26,37,38].

The linearized Freundlich isotherm equation that corresponds to the adsorption on heterogenous surface is given as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (3)$$

where C_e is the equilibrium concentration of the solute (mg dm^{-3}) and q_e is the equilibrium adsorption capacity (mg g^{-1}). The Freundlich isotherm constants K_F and $1/n$ can be calculated from the plot of $\ln q_e$ versus $\ln C_e$ (Fig. 7). The slope ($1/n$) measures the surface heterogeneity. Heterogeneity becomes more prevalent as $1/n$

Table 1
Adsorption isotherm constants for the adsorption of C.I. Disperse Orange 25 onto activated carbon from *E. rigida* by H$_2$SO$_4$ activation at various temperature

Temperature (°C)	Langmuir				Freundlich			Dubinin–Radushkevich (D–R)		
	q_{max} (mg g^{-1})	K_L (dm^3 mg^{-1})	r_L^2	R_L	n	K_F (dm^3 g^{-1})	r_F^2	q_{max} (mg g^{-1})	β (mol^2 kJ^{-2})	r_{D-R}^2
10	110.67	0.086	0.973	0.085	2.133	16.977	0.913	622.12	3.935×10^{-3}	0.921
15	117.61	0.143	0.987	0.053	2.198	23.464	0.937	694.56	3.647×10^{-3}	0.944
20	118.93	0.163	0.980	0.046	2.252	25.707	0.916	686.47	3.524×10^{-3}	0.922

Table 2
Adsorption results of disperse dye from the literature by various adsorbents

| Adsorbent	Dye	pH	Adsorbent dosage (g dm^{-3})	Adsorption capacity (mg g^{-1})
Bio-sludge [5]	Disperse Red 60	7.8	–	40.0 ± 0.1
Bio-sludge [5]	Disperse Blue 60	7.8	–	31.3 ± 3.8
Palm ash [8]	Begacron Blue BBLS (Disperse Blue)	2	5	49.50
Palm ash [8]	Miketon polyester scarlet RCS	2	5	61.35
Activated carbon from segun sawdust [29]	Disperse Blue dye	8.75	2	96.5 (% color removal)
Activated carbon from water hyacinth [29]	Disperse Blue dye	8.75	2	95.2 (% color removal)
EPI-DMA/bentonite [30]	Disperse Yellow Brown S-2RFL (DYB S-2RFL)	1.2	1	56.45
EPI-DMA/bentonite [30]	Disperse Red S-R (DR S-R)	1.2	1	53.36
EPI-DMA/bentonite [30]	Disperse Blue SBL (DB SBL)	1.2	1	49.67
EPI-DMA/bentonite [30]	Disperse Yellow (DY SE-6GFL)	1.2	1	31.83
Bentonite [31]	Disperse Red 1	–	1–10	22.73
Peat [31]	Disperse Red 1	Acidic pHs	1–10	49.73
Fly ash [31]	Disperse Red 1	Acidic pHs	1–10	30.03
Slag [31]	Disperse Red 1	Acidic pHs	1–10	33.22
Activated carbon from *Euphorbia rigida* H$_2$SO$_4$ impregnated (in this study)	C.I. Disperse Orange 25	7.0	1.2	118.93
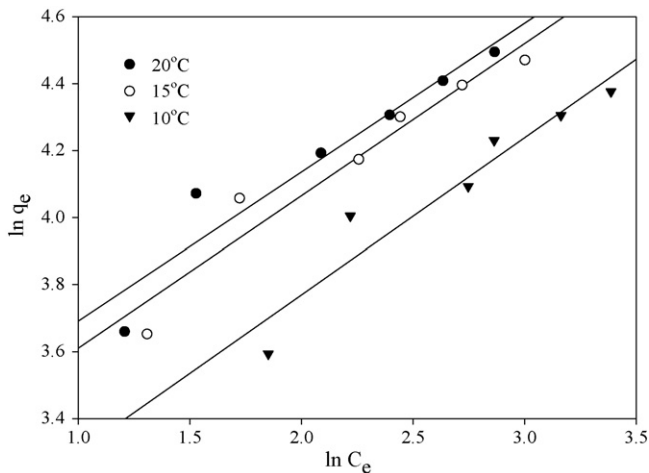
Fig. 7. Freundlich plots for the adsorption of DO25 onto activated carbon from *E. rigida*.

gets closer to zero [39]. The Freundlich constant K_F and n were influenced by temperature. Increase in temperature from 10 to 20 °C results an increase in both K_F (from 16.977 to 25.707) and n (from 2.133 to 2.252) indicating the increasing intensity of adsorption which is in confirmation with Freundlich isotherm constants (Table 1).

The D–R isotherm equation is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant adsorption potential. It was applied to distinguish between the physical and chemical adsorption of dye. The linear form of D–R isotherm equation is

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

where β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2 J^{-2}); q_m, the theoretical saturation capacity, and ε is the Polanyi potential, which is equal to $RT \ln(1 + (1/C_e))$, where R (J mol^{-1} K^{-1}) is the gas constant; and T (K), the absolute temperature. Hence by plotting $\ln q_e$ against ε^2 it is possible to generate the value of q_m (mol g^{-1}) from the intercept, and the value of β from the slope.

The D–R adsorption isotherm for DO25 onto activated carbon from *E. rigida* at different temperatures was not presented as figures due to the lower correlation coefficients than Langmuir isotherm model. The correlation coefficients showed that the Langmuir model fitted better than the other isotherm models.

3.6. Kinetics of adsorption

The kinetics of adsorption data was processed to understand the dynamics of adsorption process in terms of the order of rate constant. In order to investigate the mechanism of adsorption, the rate constants of chemical adsorption and intraparticle diffusion for DO25 were determined using the equations of a first-order [40], a pseudo-second-order [41] and intraparticle diffusion [42].

The first-order kinetic model equation is

$$\frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1}\left(\frac{1}{t}\right) \tag{5}$$

where q_1 and q_t are the amounts of the dye adsorbed at equilibrium and at time t, in mg g^{-1}, and k_1 the first-order rate constant (min^{-1}), was applied to the adsorption of DO25. Values of k_1 calculated from the slope of the plots of $1/q_t$ versus $1/t$ (figure not shown) are given in Table 3.

The pseudo-second-order kinetic model is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2}t \tag{6}$$

where q_2 is the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption, k_2 is the equilibrium rate constant for the pseudo-second-order adsorption (g mg^{-1} min^{-1}). Values of k_2 and q_2 were calculated from the plot of t/q_t against t (Fig. 8). The kinetic data for the adsorption of DO25 under various conditions were calculated from the related plots and were given in Table 3. The correlation coefficients for the pseudo-second-order kinetic model were higher than that of the first-order. An increase in the temperature also led slightly to increase in the calculated q_2 values. These results imply that the adsorption system studied obeys to the pseudo-second-order kinetic model.

The first-order and pseudo-second-order kinetic models cannot identify the diffusion mechanism and the kinetic results were then analyzed by using the intraparticle diffusion model. The intraparticle diffusion equation can be written by following:

$$q_t = k_p t^{1/2} + C \tag{7}$$

where C is the intercept, and k_p is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$).

In this part of study, intraparticle diffusion equation was applied to the adsorption of DO25 onto activated carbon from *E. rigida* as a function of the initial dye concentration and results were given in Fig. 9. According to this model, the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines

Table 3
Kinetic parameters for the adsorption of C.I. Disperse Orange 25 onto activated carbon from *E. rigida* at various temperature

	Initial dye concentration (mg dm^{-3}) (temperature: 10 °C)			Initial dye concentration (mg dm^{-3}) (temperature: 15 °C)			Initial dye concentration (mg dm^{-3}) (temperature: 20 °C)		
	75	100	125	75	100	125	75	100	125
First-order									
k_1 (min^{-1})	3.33	4.28	2.90	3.67	3.71	3.3	2.20	2.53	2.84
q_1 (mg g^{-1})	55.55	71.42	80.64	59.17	75.75	90.90	59.52	75.75	91.74
r_1^2	0.890	0.921	0.898	0.957	0.969	0.996	0.963	0.991	0.990
Pseudo-second-order									
k_2 (g mg^{-1} min^{-1})	3.92×10^{-3}	3.32×10^{-3}	3.16×10^{-3}	3.93×10^{-3}	3.33×10^{-3}	3.21×10^{-3}	5.84×10^{-3}	5.63×10^{-3}	3.49×10^{-3}
q_2 (mg g^{-1})	56.49	71.42	81.96	59.52	75.75	89.28	62.50	76.92	91.74
r_2^2	0.989	0.999	0.999	0.999	0.989	0.999	0.998	0.999	0.999
Intraparticle diffusion									
k_p (mg g min$^{-1/2}$)	0.99	1.61	1.35	1.14	1.49	1.45	0.76	1.03	1.40
C	43.67	52.57	64.93	45.64	58.32	71.60	50.64	63.81	74.79
r_p^2	0.933	0.874	0.961	0.835	0.925	0.888	0.966	0.849	0.938

(a)

(b)

(c)

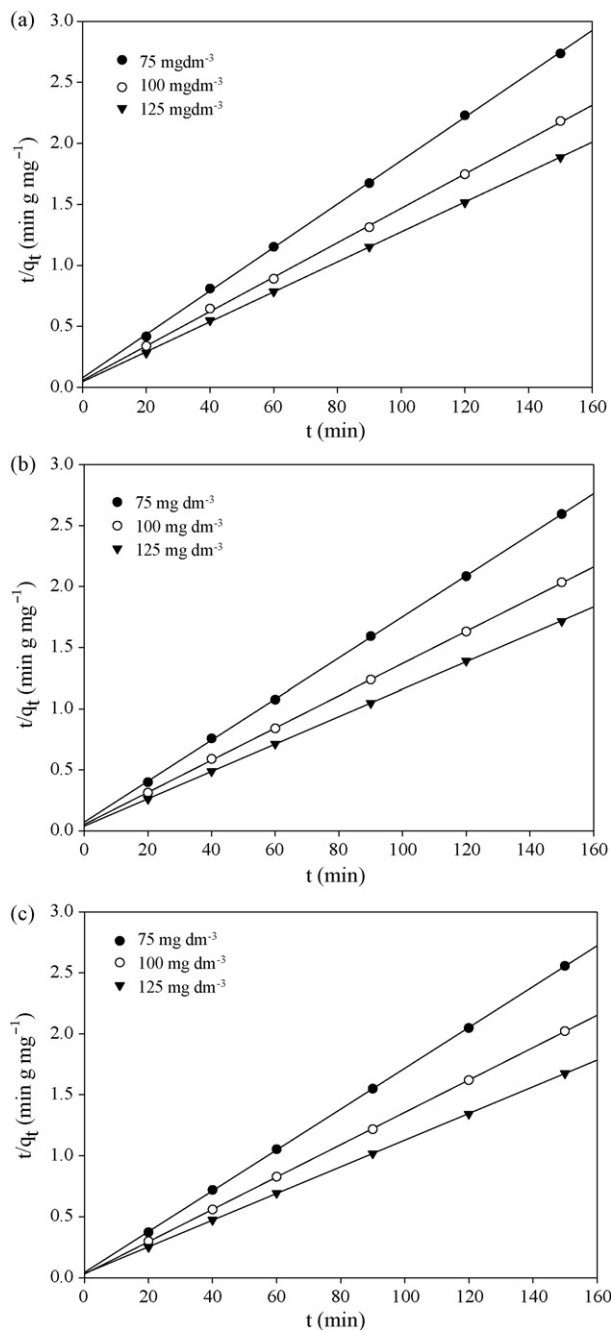**Fig. 8.** Pseudo-second-order kinetic plots for the adsorption of DO25 onto activated carbon from *E. rigida*.
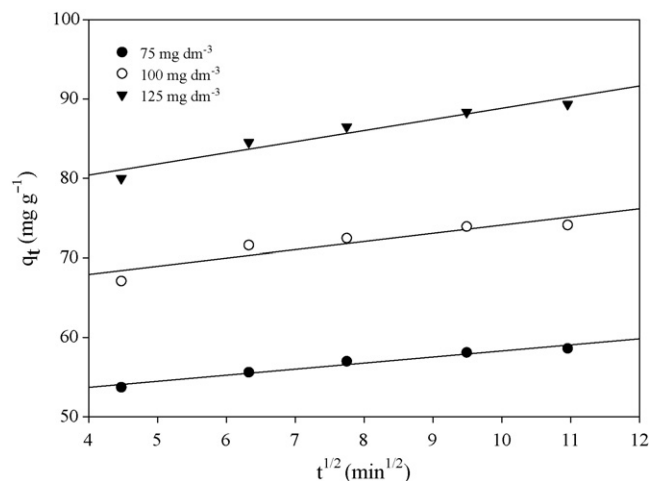

Fig. 9. Intraparticle diffusion plots for the adsorption of DO25 onto activated carbon from *E. rigida* at 20 °C.
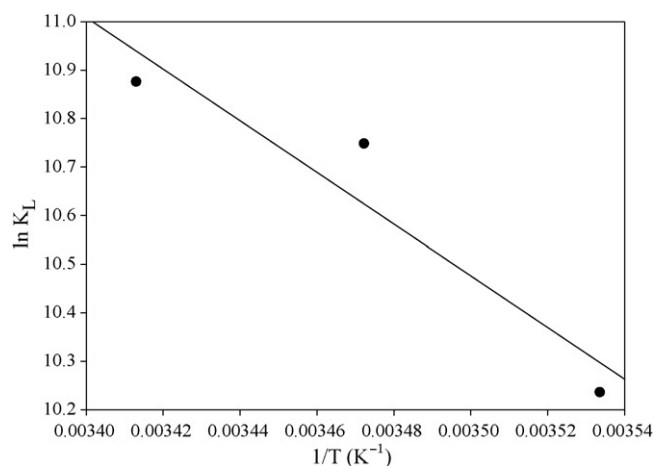

Fig. 10. Plot of $\ln K_L$ vs. $1/T$ for estimation of thermodynamic parameters for the adsorption of DO25 onto activated carbon from *E. rigida*.

Table 4
Thermodynamic parameters calculated from the Langmuir isotherm constant, K_L, for the adsorption of C.I. Disperse Orange 25 onto activated carbon from *E. rigida* by H_2SO_4 activation

t (°C)	$\Delta G°$ (kJ mol⁻¹)	$\Delta H°$ (kJ mol⁻¹)	$\Delta S°$ (J K⁻¹ mol⁻¹)
10	−24.084		
15	−25.736	44.308	242.17
20	−26.495		

pass through the origin then intraparticle diffusion is the rate-controlling step [29,40]. The plots do not pass through the origin indicating that the mechanism of DO25 adsorption onto activated carbon from *E. rigida* is complex and the actual adsorption process contains both the surface adsorption and intraparticle diffusion. The slope of linear portion from the figure can be used to derive values for the rate parameter, k_p, for the intraparticle diffusion, given in Table 3.

3.7. Thermodynamic parameters

The changes in enthalpy ($\Delta H°$), entropy ($\Delta S°$) and the free energy ($\Delta G°$), were evaluated using the equations given below [43,44]:

$$\Delta G° = -RT \ln K_L \tag{8}$$

$$\ln K_L = -\frac{\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{9}$$

The plot of $\ln K_L$ as a function of $1/T$ (Fig. 10) yields a straight line from which $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept, respectively. The results are given in Table 4.

The overall standard free energy change during the adsorption process was negative for the experimental range of temperatures (see Table 4), corresponding to a spontaneous process of DO25 adsorption. The positive value of $\Delta H°$ (+44.30 kJ mol⁻¹) confirms the endothermic nature of the overall adsorption process. This fact was previously confirmed by the isotherm experiments at different temperatures. This means that as the temperature increases, more energy is available to enhance the adsorption. The positive

entropy change (ΔS°) value (+242.17 J mol^{-1} K^{-1}) corresponds to an increase in the degree of freedom of the adsorbed species.

4. Conclusions

This study showed that H$_2$SO$_4$ impregnated activated carbon from *E. rigida* acts as a good adsorbent for the removal of DO25 from aqueous solutions. The amount of dye adsorbed was found to be dependent on solution pH, adsorbent concentration, initial dye concentration, contact time and temperature. Batch studies clearly suggest that the highest adsorption capacity of activated carbon obtained from *E. rigida* in neutral solutions (pH around 7) is 118.93 mg g^{-1} at 20 °C. Equilibrium data fitted very well in a Langmuir isotherm equation than other models. Adsorption of DO25 onto activated carbon obtained from *E. rigida* follows the pseudo-second-order kinetic and intraparticle diffusion models and they have also been applied to predict the rate constants of adsorption and adsorption capacities.

Acknowledgements

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