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ORIGINAL PAPER

Removal of crystal violet and methylene blue from aqueous solutions by activated carbon prepared from *Ferula orientalis*

T. Aysu · M. M. Küçük

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Abstract *Ferula orientalis* L. stalks were used as an agricultural solid biomass waste for preparation of activated carbon with zinc chloride activation using slow pyrolysis in a fixed-bed reactor. The chemical characteristics of the activated carbon obtained at 550 °C were identified by elemental, fourier transform infrared spectroscopy, Brunauer–Emmett–Teller, scanning electron microscopy analyses and found to have a surface area of 1,476 m^2/g. The ability of the activated carbon to adsorb methylene blue and crystal violet from aqueous solutions has been investigated. Adsorption studies were performed at different initial dye concentrations (200–800 ppm), contact time (0.5–90 min) and temperature (25–45 °C). Adsorption data were modeled with Langmuir, Freundlich and Temkin adsorption isotherms. Equilibrium data of the adsorption processes showed that adsorption of methylene blue is fitted to the Langmuir and crystal violet to the Freundlich isotherm. Pseudo-first-order, pseudo-second-order and Elovich kinetic models were used to analyze the kinetic data obtained at different initial dye concentrations. The adsorption kinetic data were very well described by the pseudo-second-order model. The calculated thermodynamic parameters such as change in free energy, enthalpy and entropy showed that adsorptions of both dyes onto activated carbon were spontaneous and endothermic under the experimental conditions.

Keywords Activated carbon · Chemical activation · Crystal violet · Methylene blue · *Ferula orientalis* L.

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Introduction

Many industries such as paper, textile, leather, food, plastics and printing use huge amounts of dyes every year to color their products worldwide. As most of these organic dyes in wastewaters are very harmful and toxic to living aquatic organisms such as fish, removal of them has become very crucial in terms of environmental concerns in recent years (Weng and Pan 2007; Vargas et al. 2011). There are several removing methods of dyestuffs from wastewaters such as oxidation, coagulation, adsorption, membrane and biological processes. Of them, adsorption seems to be the most efficient method. Activated carbon is used most widely in adsorption processes as it can be produced both from renewable and non-renewable resources with low cost (Tay et al. 2012). The low-cost activated carbons obtained from renewable agricultural wastes, and by-products so far include flamboyant pods (Vargas et al. 2011), soybean oil cake (Tay et al. 2012), cashew nut shell (Kumar et al. 2011), *Posidonia oceanic* leaves (Dural et al. 2011), date pits (Theydan and Ahmed 2012), bamboo (Hameed et al. 2007), oil palm wood (Ahmad et al. 2007), sour cherry stones (Angın 2014), date stones (Ahmed and Theydan 2012), *Jatropha curcas* fruit shell (Tongpoothorn et al. 2011), rise husks (Yalçın and Sevinç 2000), peach stones (Attia et al. 2008) and orange peel (Khaled et al. 2010).

Activated carbon can be prepared by two ways: chemical and physical activation. There are two steps in physical activation. Chemical activation, on the other hand, is carried out in one step at relatively lower temperatures than physical one. Chemical activation is defined as the pyrolysis of carbonaceous material in the presence of chemical activators such as zinc chloride, phosphoric acid or potassium hydroxide which create more micropores and higher carbon yield than physical activators (Theydan and Ahmed 2012; Li et al. 2010; Deng et al. 2011).

Methylene blue is a cationic dye which is used mostly as a colorant in textile industry such as wool, silk and cotton. It can cause eyeburns, cyanosis, tachycardia, irritation to skin, methemoglobinemia, dyspnea, irritation to gastrointestinal tract, vomiting, nausea and diarrhea in humans if contacted or ingested (Senthilkumaar et al. 2005). Crystal violet which belongs to triphenylmethane group is used widely as an animal medicine in veterinary. It is used as a biological stain to identify bloody fingerprints (Saeed et al. 2010). It is also harmful to humans and causes cancer when inhaled or ingested (Saeed et al. 2010; Ahmad 2009). It is persistent to many environments that microbial enzymes could only degrade it slightly as recalcitrant molecule (Lin et al. 2011).

Waste plant biomass can be utilized to produce activated carbon. *Ferula orientalis* L. is a perennial plant that grows in eastern Mediterranean region and central Asia. *Ferula orientalis* L. has been chosen with the idea of activated carbon production from its stalks which go dormant by midsummer and no value in terms of industrial respect. As its stalks are not used for any purpose, they can be used as a precursor for the preparation of activated carbon. This study reports the first results about the adsorption of crystal violet and methylene blue on the activated carbon obtained from *F. orientalis* L. stalks by zinc chloride activation.

The aim of the current study was to evaluate the efficiency of the removal of methylene blue and crystal violet from aqueous solutions using the activated carbon with high surface area prepared from *F. orientalis* L. stalks by zinc chloride chemical activation as a cheap and easily available adsorbent. The properties of obtained activated carbon such as surface morphology, surface area and composition were characterized by elemental, scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR) and Brunauer–Emmett–Teller (BET) analyses. The effects of contact time and temperature of dye solutions on the adsorption process were investigated to evaluate the capacity of activated carbon for maximum removal efficiency. The kinetics, equilibrium isotherms and thermodynamics of adsorption processes of dyes were investigated. This study was conducted in Van city (Turkey) in the period of December 2012 to June 2013.

Materials and methods

Preparation of activated carbon

The raw material (*F. orientalis* L.) was collected from agricultural zones between the countries of Hamur and Tutak in Ağrı province of Turkey. It was harvested in May, and the stems cleaned from leaves and tops and dried naturally in open air and then were ground, milled, and screen-sieved. Samples of different particle diameter (D_p) ranging between $0.850 > D_p > 0.425$ mm were used in this study. A total of 120 g of *F. orientalis* L. mill was mixed with zinc chloride ($ZnCl_2$) at impregnation ratio of 1:1, stirred and activated for 12 h at 25 °C. The mixture was then dried at 105 °C and stored in a desiccator. The slow carbonization (pyrolysis) of the mixture was carried out in a fixed-bed tubular reactor made of stainless steel with dimensions of 70 mm inner diameter, 10 mm outer diameter and 200 mm height equipped with connection for inert gas input. The mixture was put inside the reactor and closed tightly with connections for inert gas entry and products output pipe. The reactor was heated externally by an electric furnace, and the temperature was controlled by a NiCr–Ni thermocouple placed inside the bed. The temperature was increased by 20 °C/min from 25 °C to 550 °C at which it was kept for 30 min. During the carbonization process, nitrogen gas was circulated in the reactor with 100 cm^3/min constant flowing rate to provide the inert atmosphere inside the reactor. Then, the reactor was cooled to room temperature, and the resulting chemically activated carbon was taken and weighed. It was boiled with concentrated hydrochloric acid (HCl) to open micropores and washed with distilled water until the effluent is free from zinc ions. The resulting activated carbon was placed in funnel and filtered with distilled water for 34 days until no more chloride ions were contained in it. During the filtration, silver nitrate solution was used to check the complete removal of chloride from filtrate completely. At the end of purifying process, the obtained activated carbon was dried in an oven at 105 °C for 24 h and kept in desiccator.

Experimental procedure and adsorption isotherms

Both methylene blue and crystal violet dyes with analytical grade were purchased from Merck. One liter of 1,000 ppm stock solutions of methylene blue and crystal violet were prepared by dissolving 1 grams of each with distilled water. From these solutions, required amount is taken and diluted 250 mL with distilled water to prepare desired concentrations (200–800 ppm). Adsorption experiments performed with these solutions at three different temperatures (25, 35, 45 °C) in a glass container at a constant agitation speed rate of 250 rpm for contact time between 0.5 and 240 min by shaking in a mechanical shaker. In all trials, 0.2 g of activated carbon was used according to the parameters studied. During adsorption, 2 mL of solution was taken at different time intervals, filtered from glass wool and centrifuged. Methylene blue and crystal violet concentrations were measured before and after each trial using Boeco S22

UV–Vis spectrophotometer at 664 and 594 nm, respectively.

The equilibrium adsorption capacities (q_e) of the activated carbon were determined based on adsorbate mass balance using equation given below:

$$q_e = [(C_0 - C_e) \times V]/m \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the used dye (mg/L), respectively, V is the volume of the aqueous solution (L), and m is the mass of activated carbon used (g) (Tongpoothorn et al. 2011; Kumar et al. 2005).

Dye uptake (%A) by the adsorbent was calculated using the following equation:

$$\%A = (C_0 - C_e) \times 100/C_0 \quad (2)$$

The application of adsorption isotherms is very useful to describe the interaction between the adsorbate and the adsorbent of any system. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbent (Vargas et al. 2011). The adsorption isotherms show how the molecules distribute between the liquid and solid phases when the process reaches the equilibrium state. The analysis of the isotherm data by fitting them to various models such as Freundlich and Langmuir is an important step to find the properties and mechanism of adsorption process. It is used to find the suitable model is important for design purposes (Hameed et al. 2007; El-Guendi 1991). Three well-known isotherm equations, namely the Langmuir (Lagergren and Svenska 1898), Freundlich (Freundlich 1906) and Temkin (Igwe and Abia 2006), were applied to fit the experimental isotherm data of dyes adsorptions on the activated carbon.

The Langmuir isotherm model is based on the assumption that the adsorption process takes place on a homogeneous and monolayer surface with a finite number of identical sites, forming a monolayer of adsorbate at saturation on the adsorbent surface. The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \left(\frac{1}{q_m}\right) C_e \quad (3)$$

where q_m and K_L are the Langmuir constants related to maximum adsorption capacity and rate of adsorption, respectively. If a straight line is obtained with slope $1/q_m$ when C_e/q_e is plotted against C_e, then it indicates that adsorption of the dye on activated carbon follows the Langmuir isotherm. The Langmuir constants (K_L and q_m) can be calculated from this isotherm.

On the other hand, Freundlich presented a fairly satisfactory empirical model to describe non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption. The well-known linear form of Freundlich isotherm model is given by the following equation:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (4)$$

where n is the Freundlich constant related to adsorption intensity which indicates how favorable the process is and K_F is the Freundlich constant related to the relative adsorption capacity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon adsorbent for a unit equilibrium concentration. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghseresht and Lu 1998). A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is indicative of cooperative adsorption (Fytianos et al. 2000). If the plot of $\ln q_e$ versus $\ln C_e$ gives straight line with slope $1/n$, then it indicates that the adsorption of dye follows the Freundlich isotherm (Hameed et al. 2007).

Temkin isotherm contains a factor that explicitly taking into account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage (Tempkin and Pyzhev 1940; Aharoni and Ungarish 1977). As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity adsorbed, q_e against ln Ce and the constants are determined from the slope and intercept. The linear compact form of the model is given by the following equation:

$$q_e = B \ln A_T + B \ln C_e \quad (5)$$

where A_T is the Temkin isotherm equilibrium binding constant (L/g), and B is the constant related to heat of adsorption(J/mol). If the plot of q_e versus $\ln C_e$ gives straight line with slope B, then it indicates that the adsorption of dye follows the Temkin isotherm (Dada et al. 2012; Runping et al. 2008).

Adsorption kinetics

Adsorption kinetics is one of the most important parameters in evaluation of adsorption efficiency. Three well-known kinetic models, pseudo-first-order (Lagergren and Svenska 1898), pseudo-second-order (Ho and Mckay 1999) and Elovich (Elovich and Larinov 1962), were used in this study to analyze the kinetic data.

The pseudo-first-order kinetics is given by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (6)$$

where q_t is the amount of dye adsorbed (mg/g) at a certain time, and t is time (min) and k_1 is the pseudo-first-order rate constant (1/min). The values of the constants q_e, k_1 and R^2 are calculated from the linear plot of log $(q_e - q_t)$ versus t.

The pseudo-second-order kinetics is given by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (7)$$

where k_2 is the pseudo-second-order rate constant (g/mg min). The values of k_2, R^2 and q_e are calculated from the plot of t/q_t versus t.

The Elovich kinetics is given by the following equation:

$$q_t = \frac{1}{\beta}\ln \alpha\beta + \frac{1}{\beta}\ln t \qquad (8)$$

where β (g/mg) and α (mg/g min) are the Elovich constants corresponding to the extent of surface coverage and rate of adsorption at zero coverage, respectively. These constants are determined from the linear plot of q_t versus lnt. This equation was based on the principle, which assumed that the adsorption sites increase exponentially with adsorption (Elovich and Larinov 1962).

Adsorption thermodynamics

Thermodynamics determine the internal energy, enthalpy, entropy and free energy values of the system during physical or chemical transformation and examine how they are dependent on to the reaction conditions. Examination of the thermal events that accompany chemical reactions and the thermal properties of the reactants such as entropy and enthalpy could make it possible to put forward a general criterion about the spontaneity of the reaction and helps to obtain information about the equilibrium.

Thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are calculated by using the following equations:

$$K_d = \frac{q_{e(W/V)}}{C_e} \qquad (9)$$

$$\Delta G = -RT\ln K_\mathrm{d} \qquad (10)$$

$$\Delta G = \Delta H - T\Delta S \qquad (11)$$

Rearranging Eqs. (10) and (11) gives the linear form of the following equation:

$$\ln K_\mathrm{d} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}(\text{van}'\text{t Hoff equation}) \qquad (12)$$

where R is the universal gas constant (8.314 J/mol K), T is temperature (K), and K_d is the distribution coefficient for the adsorption, ΔG is change in free energy (kJ/mole), ΔH is change in enthalpy (kJ/mole), and ΔS is change in entropy (kJ/mol K).

ΔH and ΔS values are calculated from the slope and intercept of the linear plots of ln K_d versus 1/T. ΔG's can be determined by Eq. (11) for different temperatures. In determining the thermodynamic parameters, adsorption results of 200 ppm dye solutions were used at three different temperatures (25, 35 and 45 °C) in this study.

Results and discussion

Characterization of activated carbon

The characteristics of obtained activated carbon such as surface morphology, surface area, pore volumes and composition were determined by elemental, SEM, FT-IR and BET analyses. Ultimate analysis of the activated carbon was performed using an elemental analyzer (LECO CHNS 932). The result of elemental analysis is as follows: carbon (73.156 %), hydrogen (4.1799 %), nitrogen (1.6611 %) and oxygen (% 21.003).

FT-IR spectroscopy is an important analytical technique which detects the vibration characteristics of functional groups present on adsorbent surface. The FT-IR spectra of the activated carbon was recorded in the transmission mode between 4,000 and 550 cm^{-1} using a Perkin-Elmer Spectrum One spectrometer to identify structural groups using potassium bromide (KBr) as transparent pellet. The FT-IR spectra of the activated carbon showed peaks related to the following functional groups: 3,162.4 cm^{-1}: O–H group of phenol, 2,185.3 cm^{-1}: acetals, 1,560.69 cm^{-1}: carbonyl group, 1,056.99 cm^{-1}: C–O stretching due to the vibrations in aromatic compounds (Kumar et al. 2011).

The surface characteristics of *F. orientalis* L. activated carbon were determined by SEM. FEI Quanta 450 FEG was used to characterize the morphologies of both raw material and activated carbon. Fig. 1 shows the SEM images and EDX analyses of raw material and activated carbon, respectively. As seen from Fig. 1, the surface of raw material is smooth and has no pores on it. After $ZnCl_2$ impregnation and activation, the surface of activated carbon has become rough with many channels and pores on it. It is obvious that the impregnation with $ZnCl_2$ had very important effect on the increase in both surface area and pore volume. Besides, EDX analysis of activated carbon proves that the surface is composed of only carbon and hydrogen.

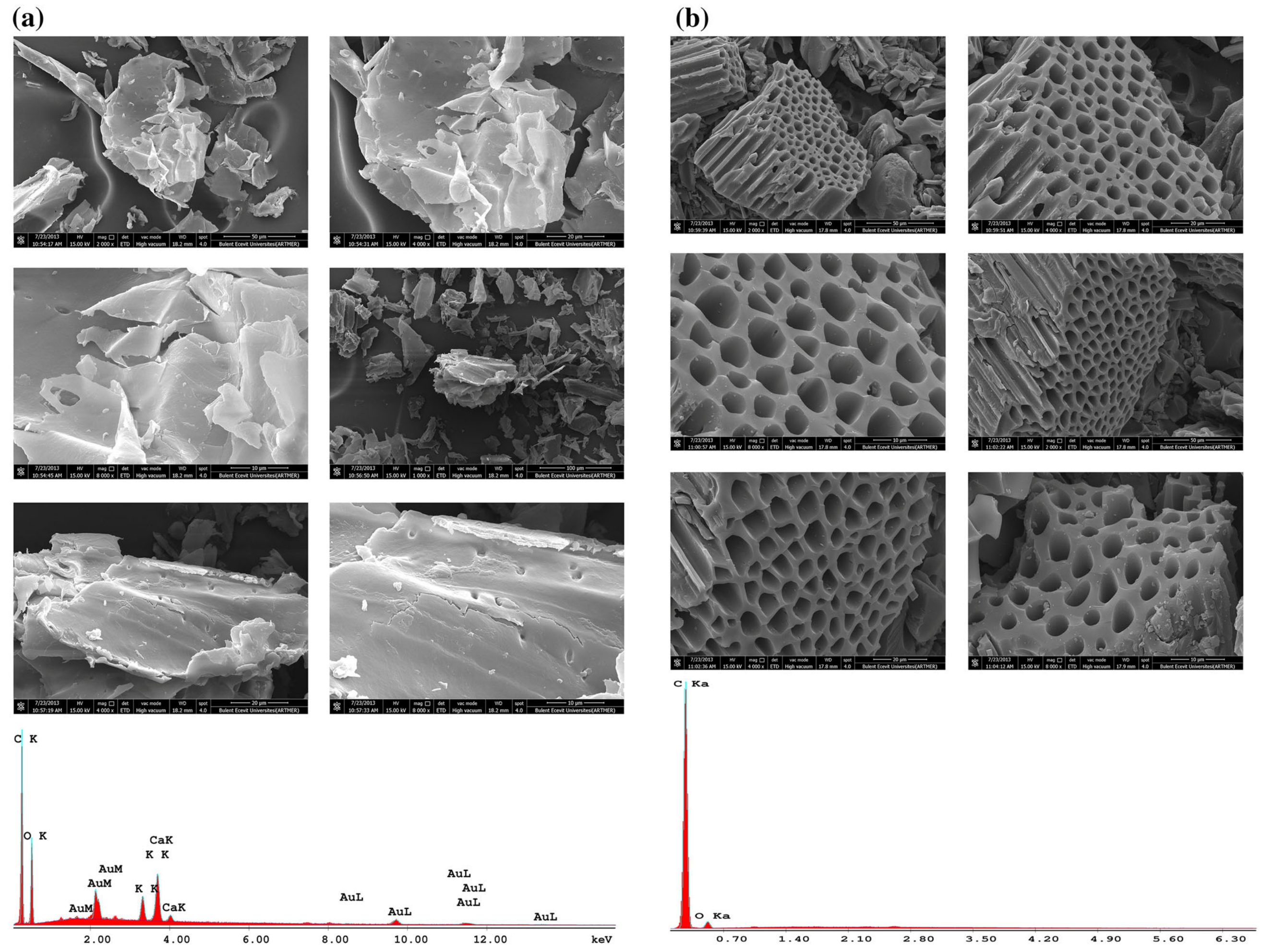


Fig. 1 SEM images and EDX analysis of **a** raw material (*F. orientalis* L.) and **b** activated carbon

Textural characterization of the activated carbon was performed by N_2 adsorption at 77 K using Quantachrome Instruments Autosorb iQ Station 2. The sample was outgassed at 553 K for 2 h before measurement. The adsorption–desorption isotherm of the activated carbon is Type I, which indicates the presence of micropores and mesopores. Surface area, pore volumes and pore sizes were analyzed from the isotherm data using various methods and given in Table 1.

Effect of contact time

To determine the effect of contact time and the time to reach equilibrium for the adsorption of methylene blue and crystal violet onto the activated carbon, 0.2 g of constant adsorbent was added to the dye solutions (250 mL) with different initial concentrations (200, 400, 600, 800 ppm) and stirred at 25 °C over a range of contact times between 0.5 and 90 min. Effect of contact time on the percent removal of both methylene blue and crystal violet is shown in Fig. 2. As seen from Fig. 2, the percent removal and adsorption capacity of both dyes were increased rapidly in the first 30 min and then slowed down until the equilibrium was reached. The optimum time for the adsorption of both dyes was observed as 50 min. After this time, the rate of adsorption was decreased gradually and reached equilibrium at 90 min, and this time was accepted as the equilibrium contact time. Increasing the contact time up to 90 min showed that the dye removal was only by about 0.6 % over those obtained for 50 min contact time. Aggregation of dye molecules with the increase in contact time makes it almost impossible to diffuse deeper into the adsorbent structure at highest energy sites. This aggregation negates the effect of contact time as the micropores are filled up and begin to resist to diffusion of aggregated dye molecules in the adsorbent. This explains the very low enhancement obtained at 90 min contact time compared to that in 50 min. After 50 min contact time, a steady-state approximation was assumed and a quasi-equilibrium situation was accepted. The adsorption curves are smooth, single and continuous leading to saturation and indicate the monolayer coverage on the surface of adsorbent bye the dye molecules (Kumar et al. 2011).

Table 1 Textural properties of the activated carbon produced from *F. orientalis* L

Surface area data (m^2/g)	
MultiPoint BET	1,476
Langmuir surface area	2,333
BJH method cumulative adsorption surface area	107.5
DH method cumulative adsorption surface area	113.2
t-method external surface area	87.16
t-method micropore surface area	1,389
DR method micropore area	1,656
DFT cumulative surface area	1,039
Pore volume data (cc/g)	
BJH method cumulative adsorption pore volume	0.1408
DH method cumulative adsorption pore volume	0.1423
t-method micropore volume	0.6480
DR method micropore volume	0.5885
HK method micropore volume	0.5984
DFT method cumulative pore volume	0.7076
Pore size data (nm)	
BJH method adsorption pore, radius (mode Dv(r))	1.814
DH method adsorption pore, radius (mode Dv(r))	1.814
DR method micropore, half pore width	0.806
DA method pore, radius (mode)	0.770
HK method pore, radius (mode)	0.183
DFT pore, radius (mode)	0.588

Kinetic data analysis

The kinetic adsorption data can be processed to understand the dynamics of the adsorption reactions in terms of the order of the rate constant since the kinetics parameters provide important information for designing and modeling the adsorption process (Vargas et al. 2011). The study of adsorption kinetics describes the solute uptake rate which controls the residence time of adsorbate uptake at the solid–solution interface (El-Sayed 2011). The mechanism of adsorption process is usually demonstrated by four steps: transport of adsorbate ions from bulk liquid to the liquid film or boundary layer surrounding the adsorbent, transport of adsorbate ions from the boundary film to the external surface of the adsorbent (surface diffusion), transfer of ions from the surface to the intra-particle active sites (pore diffusion) and adsorption of ions by the active sites of adsorbent. Because the first step is not involved with adsorbent and the fourth step is a very rapid process, they do not belong to the rate-controlling steps. Therefore, the rate-controlling steps mainly depend on either surface or pore diffusion (Theydan and Ahmed 2012).

The kinetics of methylene blue and crystal violet adsorption on the activated carbon were analyzed using pseudo-first-order, pseudo-second-order and Elovich kinetic models. The procedure used for kinetic tests was identical to that of used for equilibrium experiments. The aqueous samples were taken at different time intervals, and the concentrations of methylene blue and crystal violet were similarly measured. The adsorbed amounts of methylene blue and crystal violet at time t were calculated by the following equation:

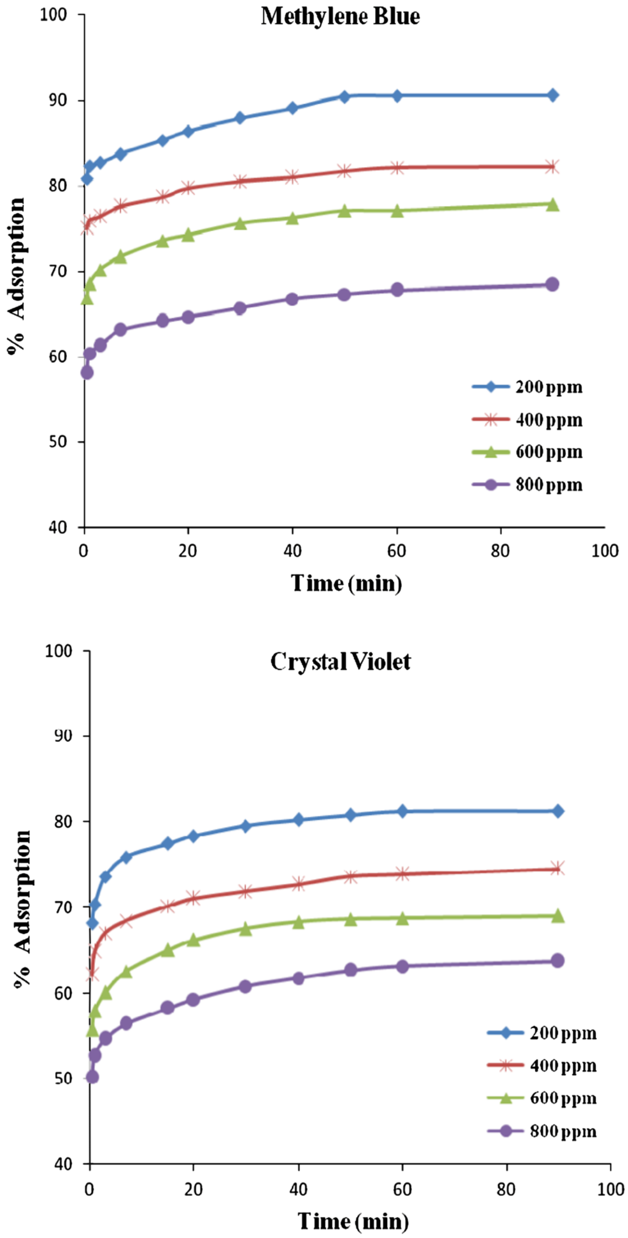


Fig. 2 Effect of contact time on the percent removal of methylene blue and crystal violet

$$q_t = [(C_0 - C_t) \times V]/m \quad (13)$$

where C_t (mg/L) is the liquid-phase concentration of methylene blue and crystal violet solution at time t (min).

Table 2 Kinetic parameters for methylene blue and crystal violet adsorption onto activated carbon at 25 °C

T(K)	q_e, exp (mg/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic			Elovich kinetic		
	Methylene blue	q_e, cal (mg/g)	k_1 (1/min)	R^2	q_e, cal (mg/g)	k_2 (g/mg min)	R^2	α (mg/g min)	β (g/mg)	R^2
	200 ppm									
298	227.5	22.9086	0.03915	0.912	227.79	0.0081	0.999	203.31	0.1997	0.918
	400 ppm									
298	411.38	37.068	0.05296	0.970	413.22	0.0062	0.999	377.31	0.1357	0.957
	600 ppm									
298	585.03	71.4496	0.04375	0.988	584.79	0.0032	0.999	511.33	0.0617	0.981
	800 ppm									
298	685.08	101.8591	0.0506	0.952	684.93	0.0026	0.999	597.78	0.0537	0.980
T (K)	q_e, exp (mg/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic			Elovich kinetic		
	Crystal violet	q_e, cal (mg/g)	k_1 (1/min)	R^2	q_e, cal (mg/g)	k_2 (g/mg min)	R^2	α (mg/g min)	β (g/mg)	R^2
	200 ppm									
298	203.21	25.9417	0.0621	0.963	204.08	0.0105	0.999	176.06	0.1532	0.992
	400 ppm									
298	373.55	49.6592	0.0437	0.986	373.13	0.0043	0.999	321.01	0.0864	0.993
	600 ppm									
298	517.75	92.4698	0.0713	0.987	520.83	0.0034	0.999	432.53	0.0486	0.989
	800 ppm									
298	642.5	110.4078	0.0345	0.986	641.02	0.0018	0.999	519.69	0.0383	0.988

The calculated constants of the three kinetics equations along with correlation coefficients, R^2 values, at different initial methylene blue and crystal violet concentrations are given in Table 2. Fig. 3 shows the curves of the three models for methylene blue and crystal violet.

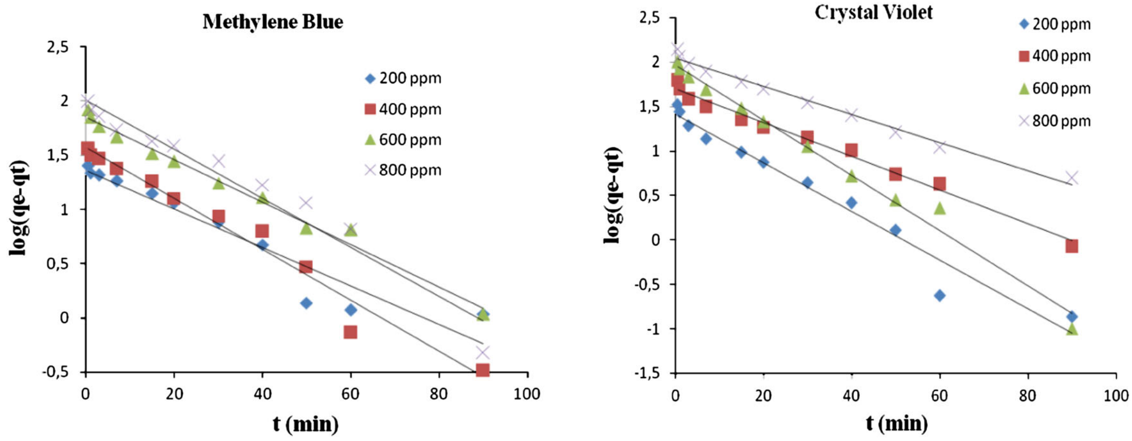
For methylene blue and crystal violet adsorption, the pseudo-first-order equation is of low correlation coefficients, R^2 values. Moreover, Table 2 shows big differences between the experimental and calculated adsorption capacities, q_e which indicates that pseudo-first-order does not fit to the experimental data for both dyes. The equilibrium adsorption capacity derived from Eq. (1) was much lower than the actual amount of equilibrium adsorption, namely 22.90, 37.06, 71.44 and 101.85 mg/g, for methylene blue with 200, 400, 600 and 800 ppm initial dye concentration, respectively. These values were 25.94, 49.65, 92.46 and 110.10 mg/g, for crystal violet with 200, 400, 600 and 800 ppm initial dye concentration, respectively.

The highest correlation coefficients, R^2 values, were obtained for the linear plot of t/q_t versus t of pseudo-second-order equation for both dyes. It can be seen that the pseudo-second-order kinetic model better fits the adsorption kinetics and the calculated q_e values agree well with the experimental qe values presented in Table 2. This suggests that the adsorptions of methylene blue and crystal violet on activated carbon follow the second-order kinetics. From Table 2, the values of rate constants, k_2, decrease with increasing initial concentrations of methylene blue and crystal violet. The reason for this behavior can be attributed to the high competition for the adsorption surface sites at high concentration which leads to higher adsorption rates (Ahmed and Theydan 2012).

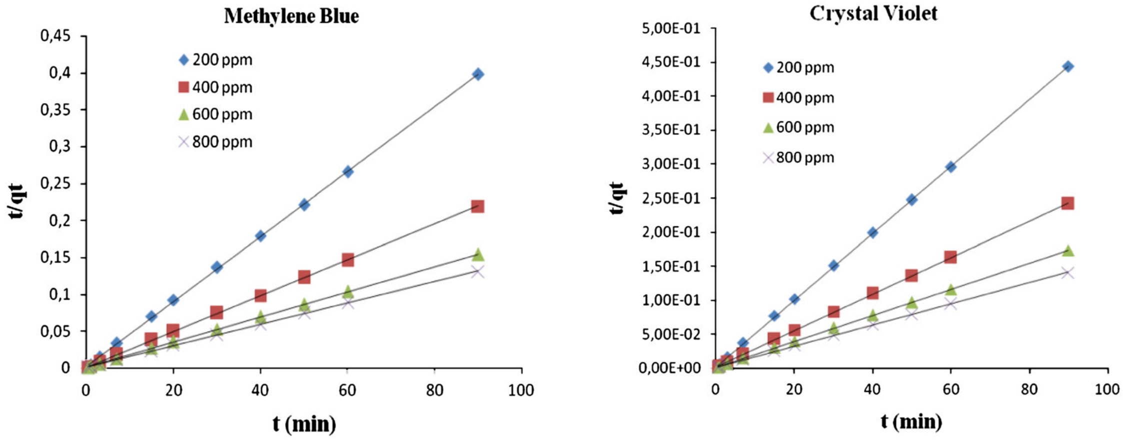
For the Elovich kinetic model, the results show a highly significant linear relationship between dyes adsorbed, q_t and ln t for both with high correlation coefficients, R^2 (>0.918). The values of R^2 for both of the pseudo-second-order and the Elovich equation are all extremely high. However, values of R^2 of the pseudo-second-order are slightly bigger than that of Elovich. From Fig. 3, it can be seen that the linear plot of t/q_t versus t of pseudo-second-order kinetics fits best and that the pseudo-second-order kinetic model better represents the adsorption kinetics. However, the linear plot of q_t versus lnt shows that the kinetic data are also fitted by Elovich kinetic model.

Isotherm data analysis

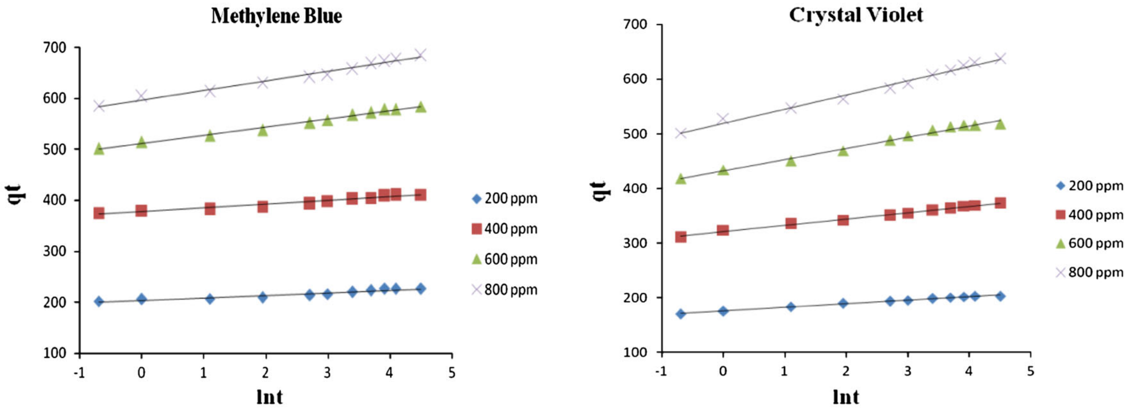
Adsorption isotherms of methylene blue and crystal violet were obtained by using 0.2 g activated carbon per 250 mL of both dye solutions at different initial concentrations ranging between 200 and 800 ppm at 25 °C. The



(a) Pseudo-first order kinetic **(a)** Pseudo-first order kinetic



(b) Pseudo-second order kinetic **(b)** Pseudo-second order kinetic



(c) Elovich kinetic **(c)** Elovich kinetic

Fig. 3 Pseudo-first-order, pseudo-second-order and Elovich kinetics for methylene blue and crystal violet adsorption onto activated carbon at different initial concentrations

Table 3 Langmuir, Freundlich and Temkin model constants and correlation coefficients for the adsorption of methylene blue and crystal violet onto activated carbon

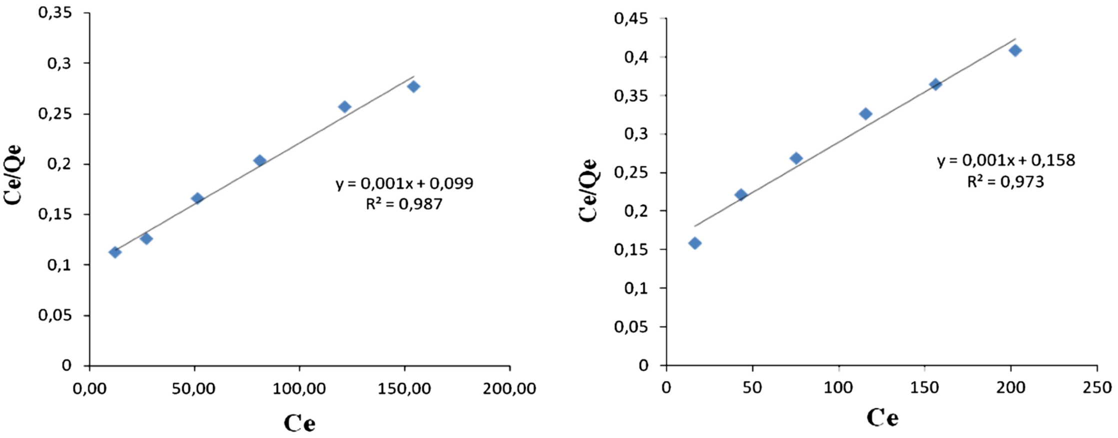
Langmuir		Freundlich		Temkin	
Methylene blue					
q_m (mg/g)	826.446	n	1.6103	B_T	171.8
K_L (L/mg)	0.01217	K_f (L/g)	25.2039	A_T (L/mg)	0.13604
R^2	0.987	R^2	0.985	R^2	0.981
Crystal violet					
q_m (mg/g)	769.2307	n	1.6077	B_T	154.9
K_L (L/mg)	0.00819	K_f (L/g)	18.4672	A_T (L/mg)	0.09686
R^2	0.973	R^2	0.999	R^2	0.961

equilibrium data were analyzed with Langmuir, Freundlich and Temkin isotherms, and the characteristics parameters of each isotherm were calculated. The Langmuir model assumes monolayer adsorption on a surface with a finite number of identical sites, whereas the Freundlich model assumes heterogeneous surface energies. The energy term in the Langmuir equation varies as a function of the surface coverage and consequently does not assume monolayer capacity. The Temkin model assumes that the heat of adsorption would decrease linearly with the increase of the coverage of the adsorbent. The applicability of the three isotherm equations was compared by evaluating the correlation coefficients, R^2 (El-Sayed 2011; Freundlich 1906; Runping et al. 2008; Langmuir 1918).

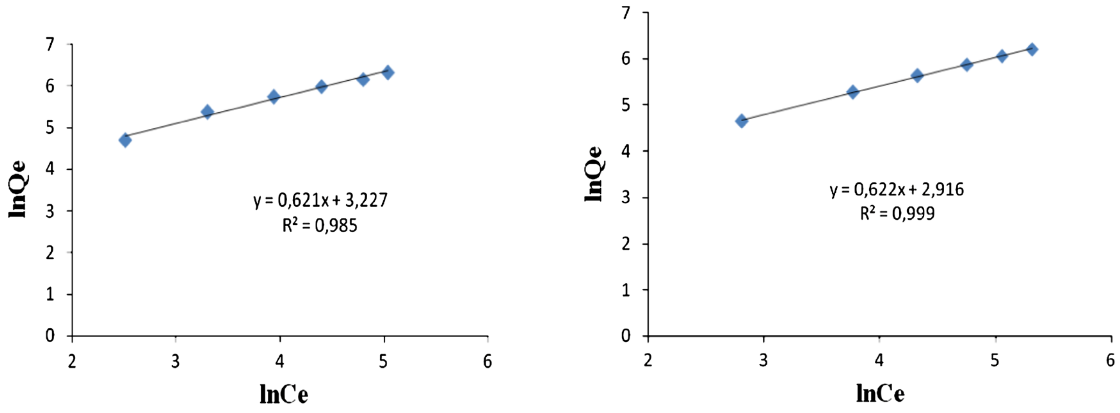
The values for the maximum amount of dyes adsorbed (q_m), correlation coefficients (R^2) and the other parameters for all three isotherms are given in Table 3. Figure 4 shows that the plot of C_e/q_e against C_e gave a straight line with slope $1/q_m$ and a 0.987 R^2 value for methylene blue. This result indicates that the adsorption of methylene blue on activated carbon follows the Langmuir isotherm and demonstrated the formation of monolayer coverage of dye molecules at the outer surface of adsorbent. The Langmuir constants K_L and q_m for methylene blue were calculated from this isotherm (Table 3). The applicability of the Freundlich adsorption isotherm was analyzed by plotting ln q_e versus ln C_e. This plot gave a straight line with slope $1/n$ and a 0.999 R^2 value for crystal violet (Fig. 4) indicating that the adsorption of crystal violet follows the Freundlich isotherm (El-Sayed 2011;Fytianos, Voudrias, and Kokkalis 2000). The n_F parameter, known as the heterogeneity factor, can be used to indicate whether the adsorption is linear ($n_F = 1$), whether it is a chemical process ($n_F < 1$), or whether a physical process is favorable ($n_F > 1$). On the other hand, the values of $1/n_F < 1$ and $1/n_F > 1$ indicate a normal Langmuir isotherm and cooperative adsorption, respectively. The Freundlich constants K_f and n for crystal violet were calculated from this isotherm. Like the Freundlich isotherm, the Temkin isotherm considers the interactions between adsorbates assuming that the adsorption heat of all molecules decreases linearly when the layer is covered and that the adsorption has a maximum energy distribution of uniform bond. The constant B_T is related to the heat of adsorption, and the positive values found ($B_T = 171.8$ for methylene blue and $B_T = 154.9$ for crystal violet) indicates an exothermic process. The fit to experimental data ($R^2 = 0.981$ for methylene blue and $R^2 = 961$ for crystal violet) in Fig. 4 shows that the Temkin isotherm is less adequate to explain the adsorption of methylene blue and crystal violet when compared to the Langmuir and Freundlich isotherms (Vargas et al. 2011).

Thermodynamic data analysis

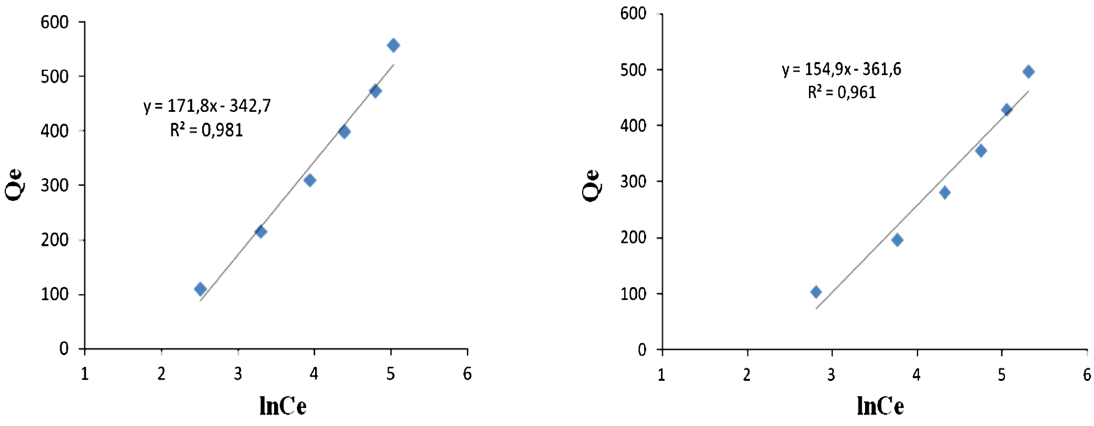
The increase in adsorption of both dyes with temperature indicates that adsorption processes of both dyes were endothermic. This can be explained thermodynamically by evaluating the parameters such as change in enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) which were calculated using the Eqs. (10) and (12). Figure 5 shows that the plot of ln Kd as a function of 1/T gave a straight line with negative slopes with the $R^2 = 0.995$ for methylene blue and $R^2 = 0.978$ for crystal violet. ΔH and ΔS values for adsorption of both dyes were calculated from the slopes and intercepts, respectively. The values of Gibbs free energy changes (ΔG) of adsorption of both dyes were calculated using the Eq. (11) which were found to be negative in the range of experimental temperatures (25–45 °C). The results of thermodynamic parameters are given in Table 4. The negative ΔG values prove that adsorption of both dyes was spontaneous and decrease in ΔG values with increasing temperature indicates that the adsorption process is more applicable at high temperatures. The positive values of ΔH for methylene blue (+6.753 kJ/mol) and crystal violet (+3.062 kJ/mol)



(a) Langmuir isotherm **(a)** Langmuir isotherm



(b) Freundlich isotherm **(b)** Freundlich isotherm



(c) Temkin isotherm **(c)** Temkin isotherm

Fig. 4 Langmuir, Freundlich and Temkin isotherms for the adsorption of methylene blue and crystal violet onto activated carbon

confirm the endothermic nature of the overall adsorption process (Gerçel et al. 2008). The positive values of ΔS (+41.486 kJ/mol K for methylene blue and +22.422 for crystal violet kJ/mol K) show the affinity of adsorbent and indicate that the two systems have an increased randomness at the solid–solution interface.

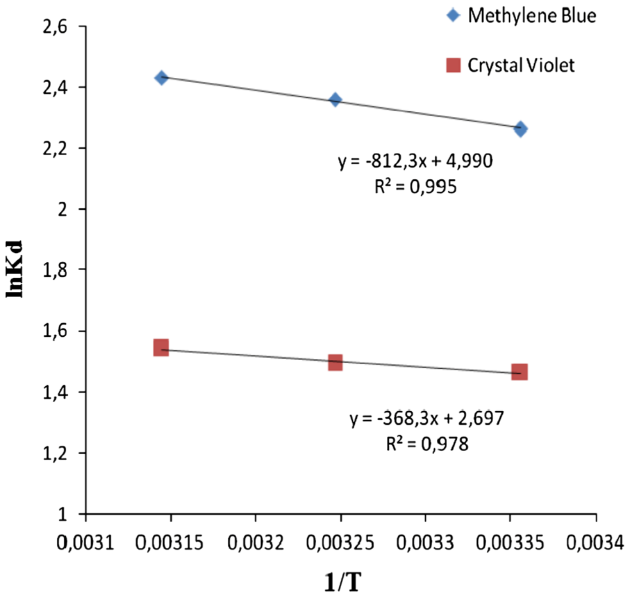


Fig. 5 Thermodynamic parameters for adsorption of methylene blue and crystal violet onto activated carbon

Table 4 Thermodynamic parameters for the adsorption methylene blue and crystal violet onto activated carbon

T(K)	lnKd	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/molK)
Methylene blue				
298	2.261	−5.603		
308	2.359	−6.042	6.753	41.486
318	2.432	−6.432		
Crystal violet				
298	1.465	−3.629		
308	1.495	−3.828	3.062	22.422
318	2.542	−4.079		

Conclusion

Ferula orientalis L. stalks were used as a precursor for the production of high surface area activated carbon by chemical activation with zinc chloride. The characteristics of the produced activated carbon as well as the adsorption capacities for methylene blue and crystal violet dyes have been studied. Methylene blue was more selectively adsorbed than crystal violet. The experimental equilibrium data for methylene blue and crystal violet adsorption onto activated carbon were well fitted to the Langmuir and Freundlich isotherm models, respectively. The kinetic of the adsorption processes was found to follow the pseudo-second-order model. The calculated thermodynamic parameters, such as $\Delta H°$, $\Delta S°$ and $\Delta G°$, showed that adsorptions of both dyes onto activated carbon were spontaneous and endothermic under the experimental conditions. The results show that activated carbons with low-cost and high surface area can be prepared from waste biomass precursors and used for wastewater treatment and water pollution control.

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