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Adsorption of Basic violet 16 from aqueous solutions by waste sugar beet pulp: kinetic, thermodynamic, and equilibrium isotherm studies

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Waste sugar beet pulp has been used as adsorbent for the removal of a hazardous cationic dye, Basic violet 16, from its aqueous solution. Adsorption of the dye was studied as function of time, pH of the solution, dosage of the adsorbent, sieve size of the particles, concentration of the dye, and temperature. The initial pH of the dye solution did not affect the chemistry of the dye molecule and the surface of beet pulp. Langmuir and Freundlich adsorption isotherms were successfully employed, and on the basis of these models, the thermodynamic parameters were evaluated. Adsorption of Basic violet 16 on beet pulp was found to be an exothermic reaction. Time contact studies showed that more than 80% adsorption of the dye is achieved in less than 1 h. Kinetics investigations confirmed both pseudo-first-order and pseudo-second-order behaviors; on the other hand, it shows that the intraparticle diffusion step is not the only rate-controlling step in all concentrations.

Keywords: adsorption; Basic violet 16; beet pulp; isotherms

1. Introduction

The environmental pollution is increasing in recent decades due to rapid industrialization and population growth throughout the world. Most of the areas situated near various industries are polluted continuously because of the disposal of industrial wastes. Water health is continuously decreasing due to addition of toxic as well as colored effluents from textile, paper, carpet, leather, distillery, printing, plastics, cosmetics, pharmaceutical, and food industries and poses severe health hazard problems.[1] Even small quantities of dyes can color large water bodies; color not only affects esthetic quality but also reduces sunlight penetration and photosynthesis.[2] In addition, some dyes are either toxic or mutagenic and carcinogenic due to the presence of metals and other chemicals, in their structure.[3–5]

Among many technique such as photocatalytic degradation, coagulation, and chemical oxidation, adsorption phenomena has proved to be a promising technology for the removal of various organic pollutants in wastewater for its many attractive advantages, including the environmental friendly feature, relatively low cost and little energy consumption. Adsorption is a method which has gained considerable attention in the recent years. It is such a useful and simple technique, which allows gathering of both kinetic and equilibrium data without needing any sophisticated instrument. Over the years, waste materials from industrial and agricultural products have been exploited as possible alternative to activated carbon to remove hazardous chemicals.[6–13]

Basic violet 16 (Figure 1) is not used as a textile dye. Instead, it is used to dye paper and as a component of navy blue and black inks for printing, ball-point pens and ink-jet printers. It is also used to colorize diverse products such as fertilizers, anti-freezes, detergents, and leather jackets.

The present work is an attempt to develop the waste pulp of sugar beet remaining from extraction of sugar as an efficient adsorbent for removal of a Basic violet 16 from aqueous solutions. The effects of pH, adsorbent dose, particle size, temperature, and initial dye concentration have been studied and obtained results are discussed.

2. Materials and methods

2.1. Materials

Basic violet 16 (with purity > 99%) was obtained from Iranian dye institute. All other chemicals (Analytical grade) such as hydrochloric acid and sodium hydroxide were obtained from Merck. Waste sugar beet (*Beta vulgaris L.*) pulp was obtained for a local sugar mill, washed with hot water, and dried. Then, it was washed with doubly distilled water and dried in oven. After grinding and dry sieving, three particle sizes were kept: 150–300, 300–600, and 600–850 μm .

FTIR (Fourier transform infrared spectroscopy) analyses with KBr disks containing finely ground sample were performed in a Perkin–Elmer RXI FTIR spectrophotometer. Infrared spectra were recorded in the region of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} .

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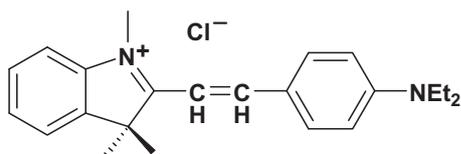


Figure 1. Chemical structure of Basic violet 16.

2.2. Adsorption studies

Adsorption of Basic violet 16 was carried out by a batch technique. Experiments were conducted to observe the effect of various parameters such as pH, temperature, particle size, amount of adsorbent, concentration, and contact time. Effect of initial pH on dye removal was studied over a pH range of 2–13. Initial pH was adjusted by the addition of dilute aqueous solutions of HCl or NaOH. The concentration of Basic violet 16 was chosen in the range of 10–80 mg L⁻¹. In order to investigate the effect of contact time, 100 mL of Basic violet 16 solution of known concentration, pH, and a known amount of the adsorbent were taken in a 2-L batch reactor circulator. The solution was vigorously stirred with a magnetic stirrer due to experimental run. In the studying of the temperature, particle size, amount of adsorbent, concentration effects, all experiments were carried out in 50 mL of the each solution in a temperature controlled shaking water bath at a constant speed of 150 rpm. Solutions were contacted with a known amount of adsorbent for 24 h till equilibrium was attained. It was observed that the 1–2 h were sufficient for establishing the equilibrium. Then, the solutions were filtered and the filtrate was analyzed spectrophotometrically for the uptake of the dye at λ_{\max} 548 nm.

2.3. Kinetic studies

Similar to contact time investigation, 100 mL of the dye solution was kept with 1.0 g of adsorbent in batch reactor circulator, while it was stirred with a magnetic stirrer at constant speed of 150 rpm. At appropriate time intervals (3 min), samples were withdrawn and centrifuged using Hettich centrifuge (model EA20) and absorbance of the sample was measured. The kinetic studies were also performed at different adsorbate concentrations (five solutions with the different concentration of the dye, 10–25 mg L⁻¹).

3. Results and discussion

3.1. Characterization of beet pulp by FTIR

Figure 2 shows the FTIR spectrum of sugar beet pulp. It confirms the special functional groups in chemical structure of beet pulp as following characteristic regions: the $\nu(\text{O-H})$ stretching bands of the hydroxyl groups around 3400 cm⁻¹; the stretching bands of the C-H (around 2900 cm⁻¹); the asymmetric and symmetric stretching

bands of the C=O around 1747 and 1644 cm⁻¹; the fingerprint region, that can be including the bands C-O of C-O-C or C-O-C of -C₅O in the cellulosic structure or the remaining sugar of beet pulp between 950 and 1200 cm⁻¹ (broad peak at 1056 cm⁻¹); and the region of the carboxyl groups (-COOH) between 1200 and 1800 cm⁻¹.

3.2. Adsorption studies

3.2.1. Effect of pH

The adsorption studies of Basic violet 16 on beet pulp at 25 °C and varying pH range (pH 2–13) showed an approximately consistent percentage removal of the dye due to pH range. Of course, a smooth increase in percentage removal of the dye was observed after pH 6. Figure 3 shows percentage removal of the dye, after 2 h, vs. pH at the room temperature. Color removal due to pH change alone may be due to the structural changes being effected in the dye molecules. Because of the special structural (Figure 3) and the lack of the protonation of Basic violet 16, effect of initial pH on the removal of the dye is negligible. Therefore, all experiments were carried out at approximate pH 4, that is, the initial pH of prepared solution.

3.2.2. Effect of particle size

Data in Table 1 show that the percentage removal of the dye has negligible tolerance with the variation of adsorbent sieve size. Therefore, the medium sieve size of particles (300–600 μm) was used in all experiments.

3.2.3. Effect of adsorbent dose

To optimize the adsorbent dose for removal of the Basic violet 16 from the aqueous solutions, adsorption was carried out with different adsorbent dosages. The dosage of the adsorbent was varied from 0.1 to 25 g/L at fixed pH, temperature, and adsorbate concentration. Figure 4 presents that percentage removal of the dye increases with increase in the amount of adsorbent. The adsorption capacity increases up to a maximum value (85.2%) in presence of 10/L dosage of the adsorbent. The increase reported was due to the increase in total surface area of adsorbent.

3.2.4. Effect of initial dye concentration

The adsorption process for Basic violet 16 was investigated at concentration ranging from 10 to 80 mg L⁻¹ at a fixed pH and at different temperatures (25, 35, and 45 °C). Figure 5 reveals adsorption of dye on adsorbent was found to increase linearly with increase in the initial concentration of the adsorbate. Uptakes of the dye at the highest concentration were nearly 13.60, 13.05, and 12.45 mg g⁻¹ (equal to removal percentage 85.0, 81.5,

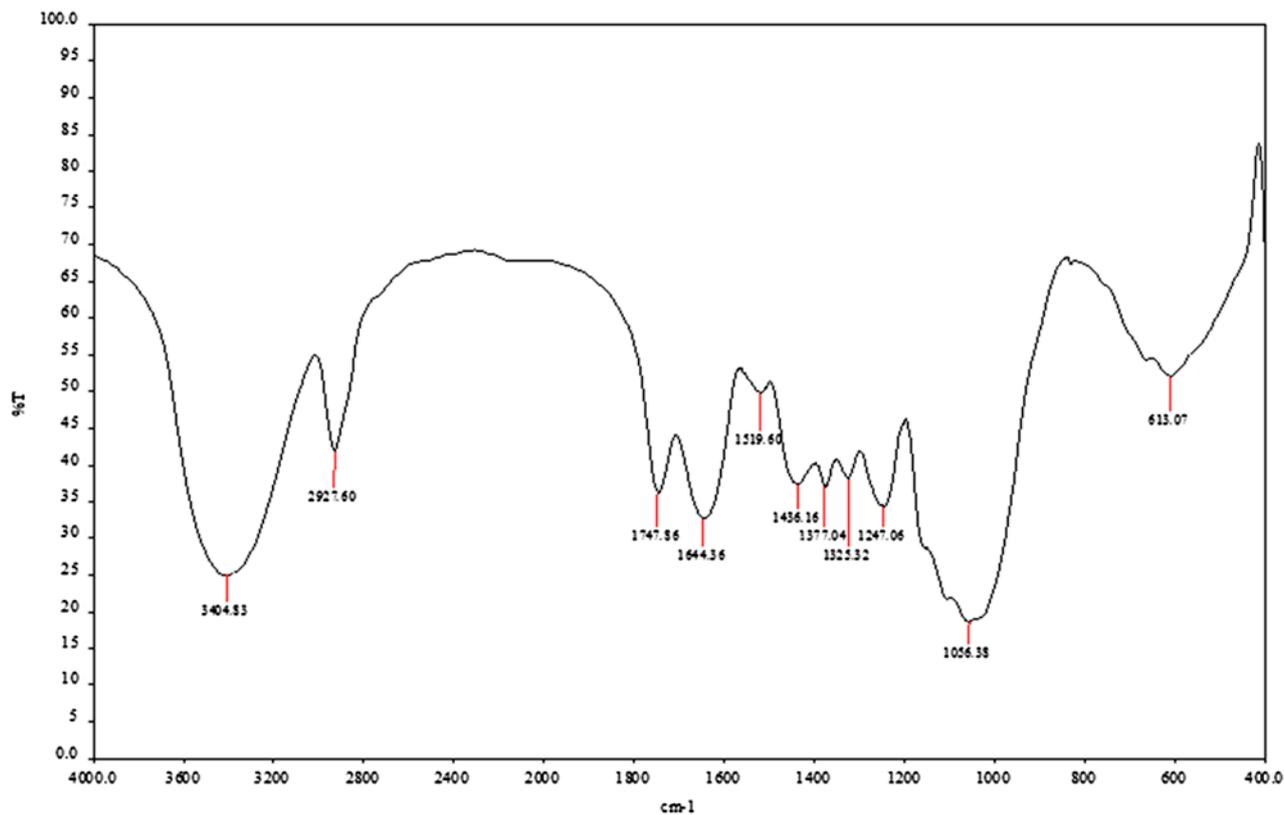


Figure 2. FTIR spectrum of the sugar beet pulp.

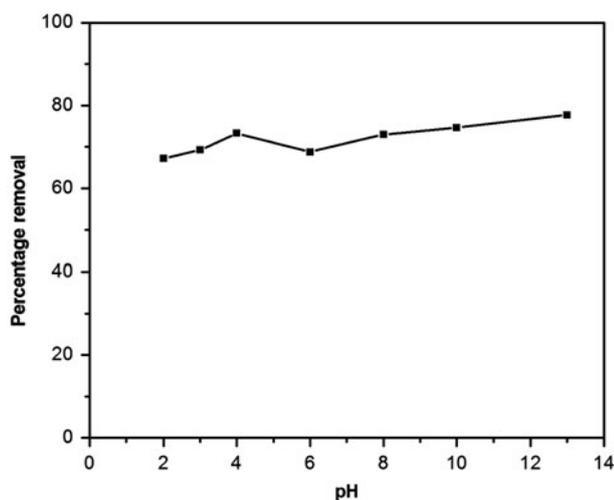


Figure 3. Effect of pH on the adsorption of Basic violet 16 over beet pulp at 25 °C. Initial concentrations of the dye and adsorbent dosage are 20 mg L⁻¹ and 10 g L⁻¹, respectively.

Table 1. Effect of adsorbent sieve size on the adsorption of Basic violet 16 at 25 °C after 24 h (initial concentrations of the dye and dosage of the adsorbent are 20 mg L⁻¹ and 1.0 g, respectively).

Sieve size/μm	150–300	300–600	600–850
Percentage adsorption	84.4	84.8	83.1

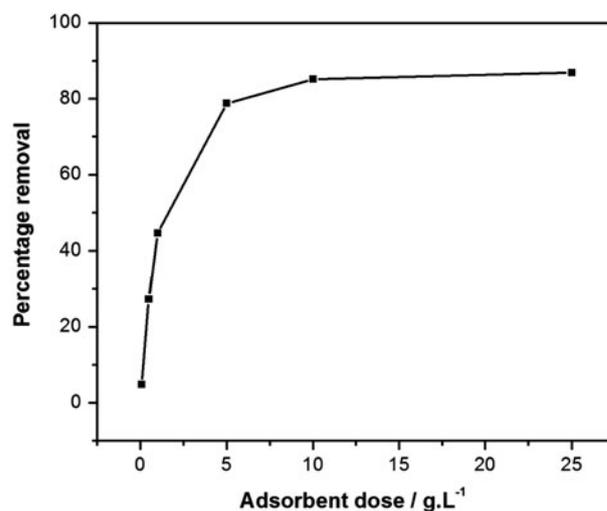


Figure 4. Effect of adsorbent dosage on the removal of the dye at 25 °C. Initial concentration of the dye is 20 mg L⁻¹.

and 77.8%) at 25, 35, and 45 °C, respectively. This decrease in adsorption indicates the exothermic nature of the process.

3.2.5. Adsorption isotherms

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the analysis and

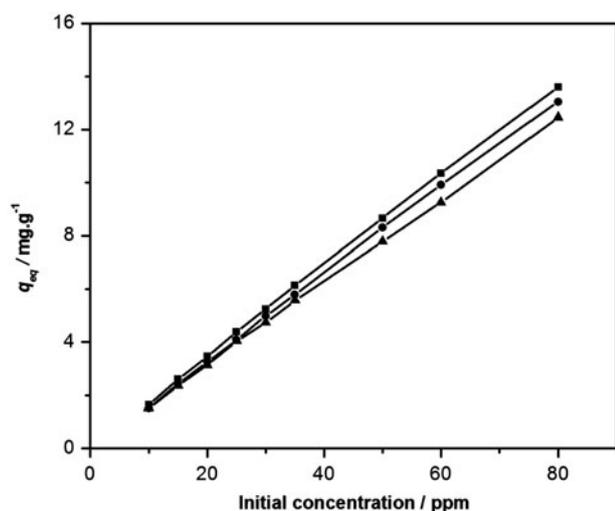


Figure 5. Effect of initial concentration on the adsorption of Basic violet 16 over beet pulp at 25 (■), 35 (●), and 45 °C (▲).

design of adsorption systems. Therefore, the experimental data points were fitted to the Langmuir and Freundlich isotherms which are the most frequently used dual-parameters equations in the literature.[14]

The Langmuir equation is valid for monolayer adsorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules. It is described by Equation (1).

$$q_{eq} = \frac{Q_0 b C_{eq}}{(1 + b C_{eq})} \quad (1)$$

where q_{eq} is the amount adsorbed, and C_{eq} is the equilibrium concentration of the adsorbate. Q_0 and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively, which are functions of the characteristics of the system as well

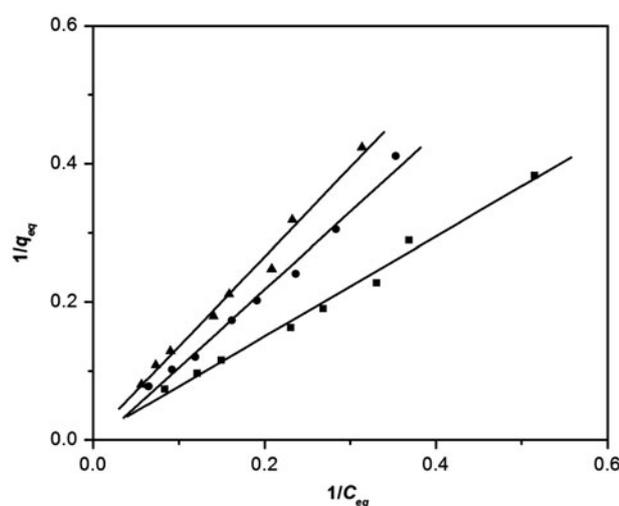


Figure 6. Langmuir adsorption isotherm of Basic violet 16 on beet pulp at 25 (■), 35 (●), and 45 °C (▲).

as time. Q_0 represents a practical limiting adsorption capacity (monolayer capacity) when the surface is fully covered with dye and assists in the comparison of adsorption performance.

When $1/q_{eq}$ is plotted against $1/C_{eq}$, a straight line with slope $1/bQ_0$ is obtained, which shows that the adsorption of Basic violet 16 can follow the Langmuir isotherm (Figure 6) for the adsorption of it on beet pulp at 25, 35, and 45 °C. Langmuir constants are calculated, and their values are given in Table 2 at studied temperatures.

The adsorption data were also found to be fitted to the linear form of the Freundlich equation

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_{eq} \quad (2)$$

where K_F and n are the Freundlich constants related to the adsorption capacity and surface heterogeneity, respectively. Figure 7 was used to calculate the Freundlich constants K_F and n for beet pulp, and their values are given in Table 2.

Table 2 shows that it was observed that the adsorption of Basic violet 16 over beet pulp fully satisfied both Langmuir and Freundlich models and straight lines were obtained in each case. This indicates uniform adsorption over the surface of the adsorbent. The value of Q_0 obtained from the Langmuir plots decreased with an increase in temperature. This also confirms that the processes are exothermic in nature. The data also show that the value of n is almost unity at all temperatures that it refers to the little heterogeneity in the surface of the adsorbent. On the other hand, surface characterizations do not change with temperature.

3.2.6. Effect of contact time

In order to innovate more effective modeling of the adsorption process, kinetics of the process was monitored. Adsorption experiments were carried out for different contact times with fixed adsorbent dose and initial concentration at pH 4 and 25, 35, and 45 °C. Figure 8 shows the effect of contact time for the removal of Basic violet 16 with respect to different temperatures under fixed initial concentration, pH, and adsorbent dose. It showed rapid adsorption of dye in the first 10 min and, thereafter, the adsorption rate decreased gradually and the adsorption equilibrium was observed in about 20 min. 80.1% of dye removal was obtained at room temperature in 20 min. Increase in contact time up to 24 h showed that removal of the Basic violet 16 by beet pulp increases only by about 7.8%. Also the adsorption rates of dye were also show an increasing with increase in temperature.

3.2.7. Adsorption kinetics

Two simplified kinetic models including pseudo-first-order and pseudo-second-order were used to test the

Table 2. Langmuir and Freundlich adsorption parameters for Basic violet 16 on beet pulp.

Temperature/°C	Langmuir parameters			Freundlich parameters		
	$Q_0/\text{mg g}^{-1}$	$b \times 10^3/(\text{mg L}^{-1})^{-1}$	R^2	$K_F/\text{mg g}^{-1}$	n	R^2
25	192.3	7.18	0.989	1.51	0.910	0.989
35	178.6	5.45	0.996	1.07	0.927	0.992
45	172.4	4.47	0.987	0.850	0.929	0.990

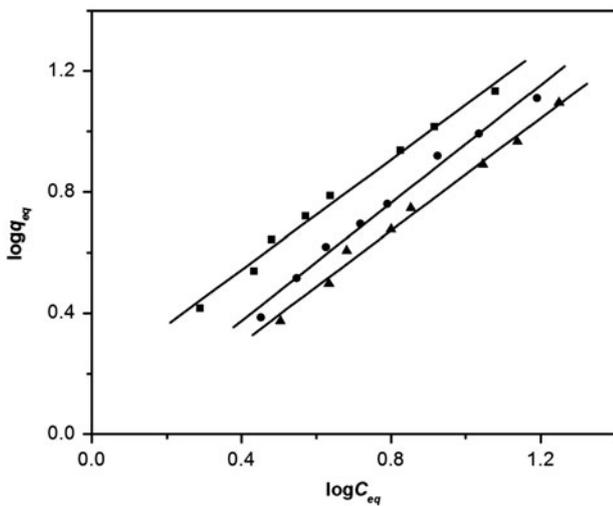
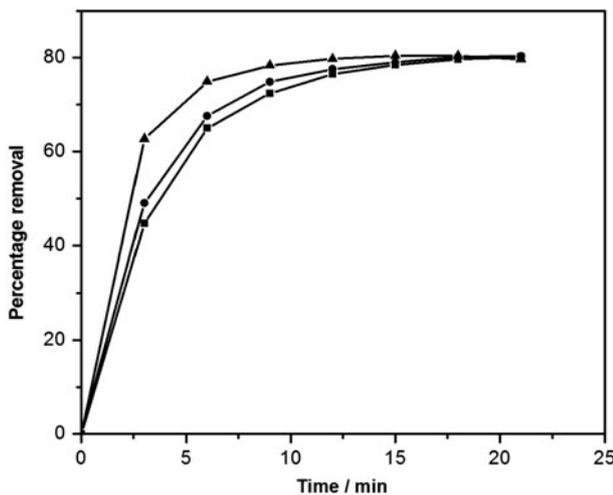


Figure 7. Freundlich adsorption isotherm of Basic violet 16 on beet pulp at 25 (■), 35 (●), and 45 °C (▲).

Figure 8. Effect of contact time on adsorption of Basic violet 16 on beet pulp at 25 (■), 35 (●), and 45 °C (▲). Initial concentration of the dye is 20 mg L⁻¹.

adsorption kinetics.[13] These two models basically include all steps of adsorption such as external film diffusion, adsorption, and internal particle diffusion. The pseudo-first-order equation is

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (3)$$

The integrated pseudo-first-order equation, the so-called Lagergren equation, with the initial condition, $q_t = 0$ at $t = 0$ leads to:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303t} \quad (4)$$

where q_t is the amount of adsorbate adsorbed at time t , q_e is the adsorption capacity in equilibrium, k_1/min^{-1} is the pseudo-first-order rate coefficient, and t is the contact time.

The pseudo-second-order equation is expressed as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where $k_2/\text{g mg}^{-1} \text{ min}^{-1}$ is the rate coefficient of second-order adsorption. The integrated form of Equation (5) becomes

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right) t \quad (6)$$

Kinetic studies were carried out using five solutions with the different concentration of the dye, 10–25 mg L⁻¹, at 25, 35, and 45 °C. The plots were linear for both pseudo-first-order and pseudo-second-order

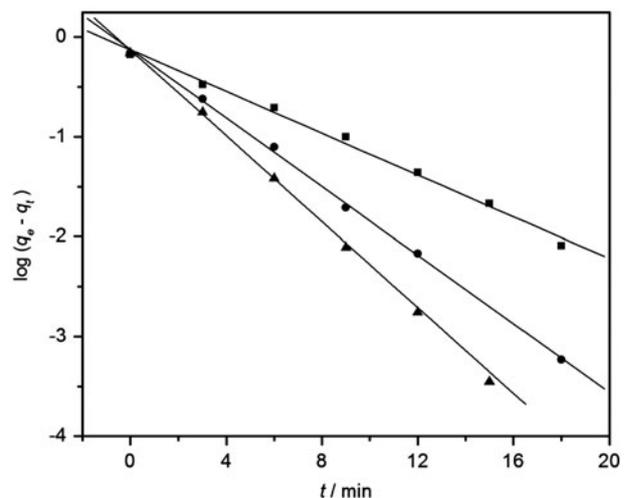


Figure 9. Kinetic plots for the adsorption of Basic violet 16 over beet pulp based on pseudo-first-order model at 25 (■), 35 (●), and 45 °C (▲).

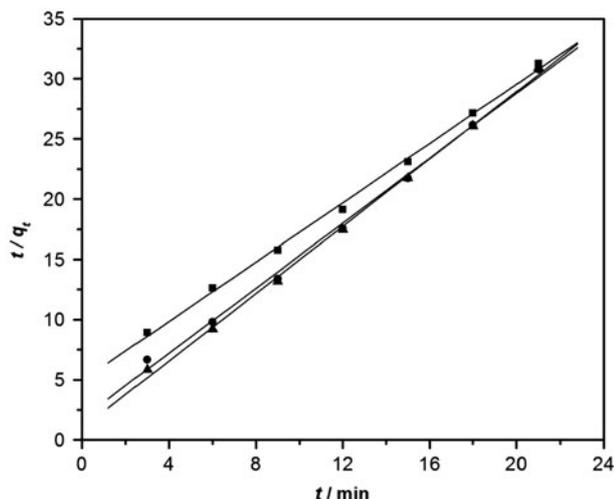


Figure 10. Kinetic plots for the adsorption of Basic violet 16 over beet pulp based on pseudo-second-order model at 25 (■), 35 (●), and 45 °C (▲).

models. Figures 9 and 10 show the linear behavior of the kinetic data in the solutions. The k_1 and k_2 values evaluated from two kinetic models are presented in Table 3. The closeness among the experimental values with the different kinetics models show that there is not explicit difference between pseudo-first-order and pseudo-second-order model and both models can be acceptable hypothesis.

3.2.8. Intraparticle diffusion

During the adsorption process, adsorption occurs at the outer surface of the adsorbent. The dye diffuses from the bulk of the solution into the pores of the adsorbent and condenses on the wall. Adsorption rate of the dye onto the adsorbent particles depend on the rate of mass transport processes of the dye within the pores of solid particulates by diffusion. The intraparticle diffusion rate of the dye is investigated by Equation (7) [15]:

$$q_t = k_i t^{1/2} + \theta \quad (7)$$

where $k_i/\text{mg g}^{-1} \text{min}^{-0.5}$ is the intraparticle diffusion rate constant. The θ is a constant depend on boundary layer. Usually, linear behavior of q_t vs. $t^{1/2}$ shows two different slopes. It evidences a dual step mechanism for adsorption process including the adsorption of the dye on outer layer of the surface and then diffusion of the molecules into the pores of the adsorbent. Figure 11 shows plot of q_t vs. $t^{1/2}$ according to Equation (7). The initial steeper

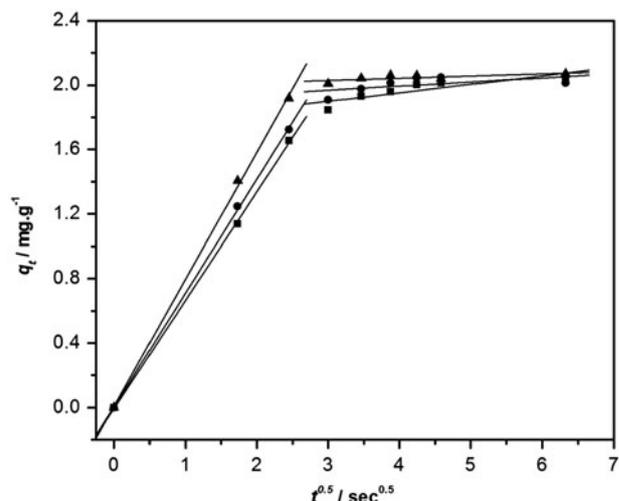


Figure 11. Plots of amount of the dye adsorbed (q_t) vs. $t^{1/2}$ based on intraparticle diffusion model at 25 (■), 35 (●), and 45 °C (▲).

section represents surface or bulk diffusion, and the second linear section represents a gradual adsorption stage where intraparticle or pore diffusion is rate limiting. As the plot did not pass through the origin, intraparticle diffusion was not the only rate-limiting step. Thus, there were two processes controlling the adsorption rate but only one was rate limiting in any particular time range. The k_i and intercepts values were obtained from the second section of the linear of the curves in different temperatures and shown in Table 3.

3.2.9. Thermodynamic parameters

Various thermodynamic parameters were also calculated for adsorption process using following equations:

$$\Delta H^\circ = -R \left(\frac{\partial \ln b}{\partial (1/T)} \right) \quad (8)$$

$$\Delta G^\circ = -RT \ln b \quad (9)$$

$$\Delta S^\circ = - \left(\frac{\partial \Delta G^\circ}{\partial T} \right) \quad (10)$$

where ΔH° is the change in enthalpy, ΔS° the change in entropy, ΔG° the change in Gibb's free energy and b the Langmuir constant. The obtained values of the thermodynamic parameters are given in Table 4. The negative value of ΔH° confirms that the adsorption process of

Table 3. Rate coefficients and intraparticle parameters for the adsorption of Basic violet 16 on beet pulp at different temperature.

Temperature/°C	k_1/min^{-1}	$k_2/\text{g mg}^{-1} \text{min}^{-1}$	$k_i/\text{mg g}^{-1} \text{min}^{-0.5}$	$\theta/\text{mg g}^{-1}$
25	0.264 ± 0.025	0.779 ± 0.297	0.0525	1.74
35	0.339 ± 0.021	0.812 ± 0.332	0.0252	1.89
45	0.428 ± 0.060	0.838 ± 0.340	0.0138	1.99

Table 4. Thermodynamic parameters for the adsorption of Basic violet 16 on beet pulp.

$\Delta G^\circ/\text{kJ mol}^{-1}$			$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
25 °C	35 °C	45 °C		
12.230	13.347	14.304	-18.696	-103.69

Basic violet 16 on beet pulp is exothermic in nature and physical nature of the adsorption.

4. Conclusion

The present study shows that the beet pulp is an effective adsorbent for the removal of Basic violet 16 from aqueous solutions. The effect of initial pH on the removal of the dye is negligible. The adsorption of the dye on beet pulp followed both pseudo-first-order and pseudo-second-order kinetics. The adsorption mechanism was found the rate-limiting step was mainly surface adsorption including bulk diffusion and intraparticle diffusion processes. Adsorption process satisfies the Langmuir adsorption isotherm and thermodynamic parameters show that this process is exothermic and physical in nature. Of course, results refer to the homogeneity in the surface of the adsorbent and an ideal adsorption process.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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