

Adsorption of Basic Dyes from Aqueous Solution by Various Adsorbents

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ABSTRACT

Activated clay, montmorillonite, and activated carbon were used for the removal of two basic dyes, Basic Green 5 (BG5) and Basic Violet 10 (BV10). Both dynamic and equilibrium data were obtained by the batch technique. The dynamic data indicate that the activated carbon was suitable for BG5 but not for BV10 primarily due to the molecular structure, whereas the montmorillonite was not good for either basic dye due to its low surface area for adsorption. The adsorption process was analyzed in terms of two pseudosteady-state equations and the intraparticle diffusion model. The adsorption isotherms of Langmuir and Freundlich as well as Langmuir–Freundlich types were employed to examine the equilibrium adsorption data. Results show that all the adsorption systems could be

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adequately fitted by the Langmuir–Freundlich equation. Thermodynamic parameters were also obtained.

Key Words: Activated carbon; Activated clay; Montmorillonite; Adsorption; Basic dyes.

INTRODUCTION

Dyes are widely used in many industries, mainly in textile industry. Their effluents often cause serious environmental problems due to deep color present in the discharge water that requires pretreatment for color prior to disposal into a river. Due to large amounts of metal complex present in the dyes, most commercial dyes are treated with difficulty by the conventional biodegradation or chemical oxidizing method. Liquid-phase adsorption of dyes from discharge streams by various adsorbents becomes one of the major treatments for such wastewater because this process is simple, inexpensive, and easy to design. Activated carbon, due to its effectiveness, is the most widely used adsorbent. Many researches^[1–5] have conducted a great number of studies on the adsorption of dyes onto activated carbon.

With the exception of activated carbon, the use of other low-cost adsorbents has also been the focus of recent research. These include silica gel, clays, sawdust, bagasse pith, peat, and fly ash.^[6–17] Activated clay and montmorillonite are porous matrix materials, mainly containing silica and aluminum. Both clay minerals are inexpensive. Activated clay and acid-treated activated montmorillonite have been used widely in the decoloration process in the cooking oil industry.^[18,19] However, their uses in the adsorption of dyes in aqueous solution have not been well documented. Wu et al.^[11] and El-Geundi et al.^[12,13] reported that basic dye can specifically be adsorbed onto activated clay. Hsu et al.^[15] found activated clay to have an excellent affinity for basic dyes and the degree of adsorbability depends greatly on the species of basic dyes, temperature, and relative concentrations of the adsorbate and adsorbent.

A comparison study on the adsorption of dyes onto activated clay, montmorillonite, and activated carbon has not yet been reported. The aim of this study is to compare the adsorption behavior of basic dyes onto activated clay, montmorillonite, and activated carbon from aqueous solution, including their dynamic and equilibrium behaviors. Dynamic adsorption models and adsorption isotherm models were also justified. The effect of temperature on dye adsorption was also examined.



EXPERIMENTAL

Materials

The dyes used in this study were Basic Green 5 (BG5) and Basic Violet 10 (BV10), supplied by Acros Chemical Company and were used without further purification. The BG5 is a relatively smaller basic dye with a linear structure and having molecular weight of 364.5, while BV10 is relatively larger with a molecular weight of 478.5. The adsorbents used were activated clay purchased from Laporte Industries (Singapore) Pte., Ltd., montmorillonite purchased from the Aldrich Company, and activated carbon purchased from a local source in Taiwan. Activated clay and activated carbon were used as received and montmorillonite was treated with diluted nitric acid for 3 hr for activation before use. The BET surface area was measured to be 278.4, 165.05 and 945.88 m²/g for activated clay, montmorillonite, and activated carbon, respectively. Their pore size distributions are shown in Fig. 1. This figure

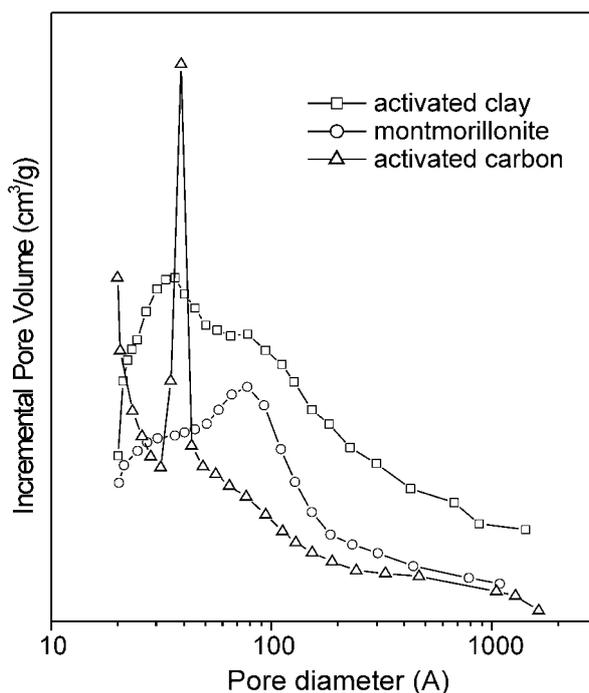


Figure 1. Pore size distribution of three adsorbents.



shows that for the activated carbon there are two peaks, 0–20 and 35–45 Å, which are located in the micropore and mesopore ranges, respectively, while for the other two adsorbents there is only one peak, 35–45 Å. Apparently, activated carbon possesses more micropores and surface area.

Synthetic dye wastewater was prepared by dissolving the different basic dyes in deionized water at proper concentration.

Adsorption Procedure

All adsorption studies were conducted in a cylindrical plastic tank with a volume of 1500 cc to obtain dynamic and isotherm data. For the dynamic experiments, a 500 cc volume of synthetic dye solution with desired concentration was first placed in the tank at desired pH, agitation, and temperature. The timing was started upon the addition of 1.0 g adsorbent. At fixed time intervals, a sample of 10 cc was taken and immediately filtered. The concentration of dyes in each sample was analyzed using a Shimadzu UV/VIS spectrophotometer (model UV-160A) at a suitable wavelength. The calibration curves for each individual dyestuff were established.

In isotherm experiments, 1.0 g of adsorbent and 500 cc of an aqueous solution with desired concentration of dye were placed in the tank at pH 3.0 and desired temperature for 3 hr. After filtration, the concentration of dye in the aqueous solution was measured.

RESULTS AND DISCUSSION

Effect of Agitation Speed

In a liquid adsorption system, the transfer rate of a solute to a particle is affected by liquid film thickness surrounding the particle and the film thickness depends on agitation speed. A series of experiments at different degrees of agitation (from 200 to 600 rpm) were undertaken and shown in Fig. 2 for the adsorption of BG5 on activated clay. Figure 2 indicates that the degree of agitation influences the sorption rate as the agitation rate increases from 200 to 600 rpm. At agitation rates higher than 400 rpm the sorption rates only differ to a quite small extent, indicating that the film thickness has insignificant effect when the agitation rate is higher than 400 rpm. Hence, an agitation rate of 500 rpm was selected for all the experiments.



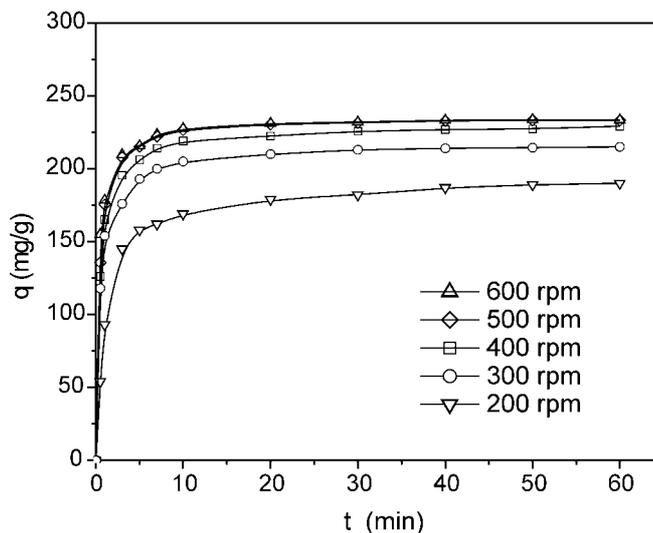


Figure 2. Effect of agitation speed on the adsorption of BG5 on activated clay with $C_0 = 700 \text{ mg/dm}^3$.

Effect of Initial Concentration

The adsorptions of BG5 on activated carbon with different initial dye concentrations are shown in Fig. 3. The adsorption capacity near equilibrium increases from 146 to 268 mg/g with an increase in the initial dye concentration from 300 to 700 mg/dm³. Similar trends were observed for the other adsorption cases, indicating that the adsorption capacity increases with increasing initial dye concentration within the operation conditions in this study. Figure 3 also indicates that the initial adsorption rate increases with increasing initial dye concentration as well.

Adsorption Dynamics

The dynamic adsorptions of the two dyes, BG5 and BV10, during the adsorption process by the three adsorbents are shown in Fig. 4 with an initial dye concentration of 700 mg/dm³. It was found that all the adsorptions have quite high initial uptake. More than 80% of the adsorption is completed within the first 10 min of contact. This is primarily due to strong electrostatic attraction between adsorbate and adsorbent. The adsorption then gradually reached a relative constant value, i.e., equilibrium adsorption. Figure 4 also indicates that the activated carbon has much faster initial adsorption rate than do the other two



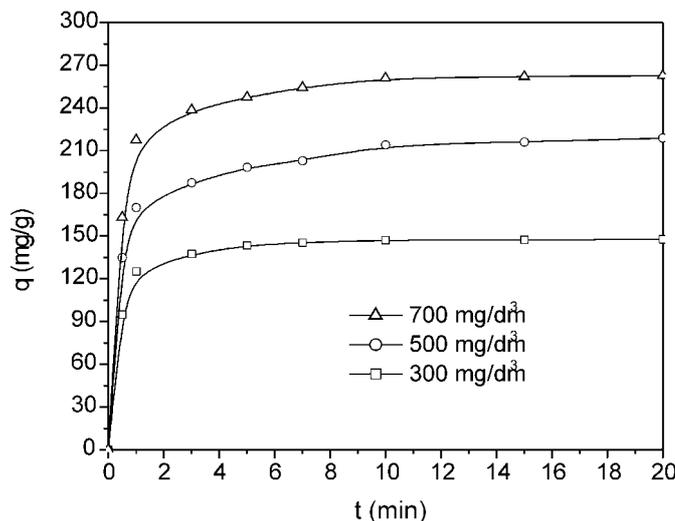


Figure 3. Effect of initial concentration on the adsorption of BG5 on activated carbon.

adsorbents for both dye adsorptions. The order of adsorption capability of adsorbents for BG5 is activated carbon > activated clay > montmorillonite, while for BV10 the order is activated clay > montmorillonite > activated carbon although they are relatively close. Another interesting point is that the activated carbon presents much better adsorption capability for BG5 than for BV10. This result can be explained by the different structure of dyes and the micropores possessed by the activated carbon. Usually dye ions have a tendency to aggregate in solution and dyes are adsorbed with an aggregation extent proportional to the cube of the ionic weight of the dye.^[17] Since BV10 is a relatively larger molecule as compared to BG5, it may aggregate to a much larger adsorbate, which could be too large to enter the micropores within the activated carbon, causing the available adsorption surface area to be drastically reduced.

A suitable model is needed to describe the adsorption process, which may involve mass transfer and chemical reaction. Many models have been proposed for this process.^[20-26] Some of them are based on reaction kinetics. A simple kinetic analysis is the pseudo first-order adsorption model:

$$\frac{dq}{dt} = k_1(q^* - q) \tag{1}$$

Integrating this equation with initial condition $q = 0$ at $t = 0$ gives

$$\ln(q^* - q) = \ln q^* - k_1 t \tag{2}$$



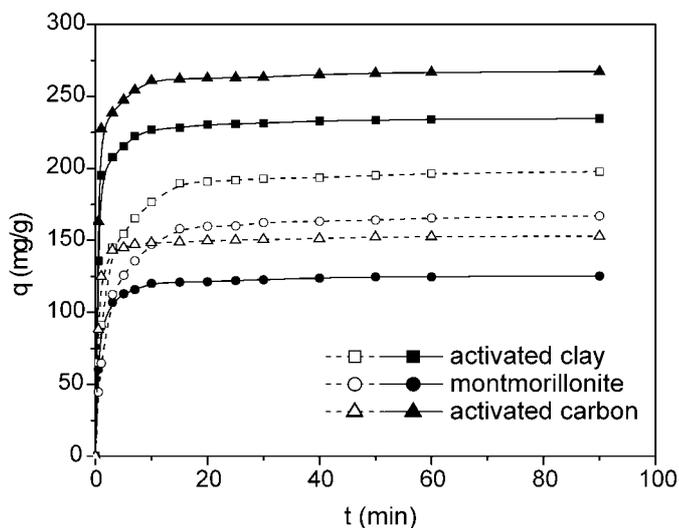


Figure 4. Adsorption kinetics of basic dyes onto three adsorbents (on the basis per weight of adsorbent). (Filled for BG5 and open for BV10.)

where k_1 is the pseudo first-order rate constant and q^* is the equilibrium dye concentration. The intercept of the straight-line plot $\ln(q^* - q)$ against t should equal $\ln q^*$.

Another kinetic analysis is the pseudo second-order adsorption model:

$$\frac{dq}{dt} = k_2(q^* - q)^2 \tag{3}$$

where k_2 is the pseudo second-order rate constant. Integration of Eq. (4) yields

$$\frac{t}{q} = \frac{1}{(k_2q^{*2})} + \frac{t}{q^*} \tag{4}$$

Plotting t/q against t yields a straight line with a slope equal to $1/q^*$ and intercept equal to $1/k_2q^{*2}$.

Figures 5 and 6 display the plots of $\ln(q^* - q)$ vs. t and t/q vs. t for various adsorbents at initial concentration of 700 mg/dm^3 . Apparently, the experimental data follow reasonably well the linear relationship of the pseudo second-order adsorption model instead of the pseudo first-order adsorption model. As time approaches to zero, according to the pseudo second-order model, the initial adsorption rate, h (mg/g min) is:

$$h = k_2q^{*2} \tag{5}$$



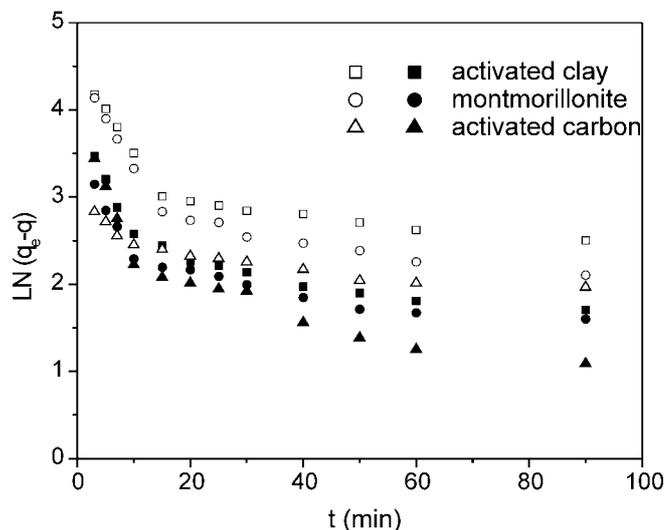


Figure 5. Test of pseudo first-order equation of basic dyes on three adsorbents. (Filled for BG5 and open for BV10.)

The k_2 , q^* , and h values for these six adsorption systems are tabulated in Table 1, using the least square method as the calculating tool. Table 1 shows that the initial adsorption rates, h , for activated carbon are high and are low for montmorillonite.

The intraparticle diffusion model is also tested by plotting the amount of adsorbed dye q against the square root of time $t^{1/2}$.^[15,25,26] Figure 7 shows such result for BG5 and BV10. In this plot we see three clear adsorption stages for all the adsorption cases. The first stage is an instantaneous adsorption and is a quick uptake stage. This plot indicates that the first stage corresponds to more than 80% adsorption and is probably due to strong electrostatic attraction between dyestuff and external surface as well as surface of larger pores. Also, the initial adsorption rates revealed from this figure are comparable with those obtained from the second pseudo steady-state model. The second stage is a gradual adsorption stage. This stage can be attributed to intraparticle diffusion, i.e., dye molecules diffusion through smaller pores. It is interesting to see from Fig. 7 that the uptake of BV10 by activated carbon at this stage is quite small as compared to the other adsorption cases, indicating that the diffusion of BV10 within the activated carbon is hindered. This is probably due to smaller micropores inside the activated carbon that are too small for BV10 to enter. The final stage is an equilibrium adsorption. At this stage, almost all active sites of the adsorbent are occupied by dye molecules. This section also

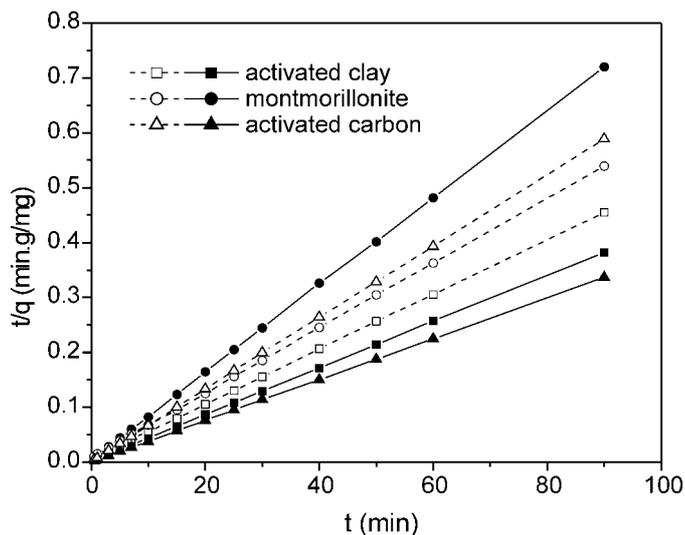


Figure 6. Test of pseudo second-order equation of basic dyes on three adsorbents. (Filled for BG5 and open for BV10.)

corresponds to the maximum adsorption of dyes for the specified experimental conditions.

Adsorption Isotherm

Figures 8 and 9 illustrate the adsorption isotherms of BG5 and BV10 on the three adsorbents, a plot of amount of dye adsorbed per unit mass of adsorbent (q_e) vs. equilibrium concentration of dye in liquid phase (C_e). It was

Table 1. Comparison of k , q^* , and h values of the pseudo second-order adsorption model for various adsorbents and adsorbates.

Adsorbate	Adsorbent	q^*	$k_2 \times 10^3$	h
BG5	Activated clay	236	9.47	527
	Montmorillonite	126	13.64	215
	Activated carbon	268	11.86	852
BV10	Activated clay	200	4.15	166
	Montmorillonite	170	3.92	113
	Activated carbon	153	17.91	421

Note: q^* (mg/g); k_2 (g/mg.min); h (mg/g min).



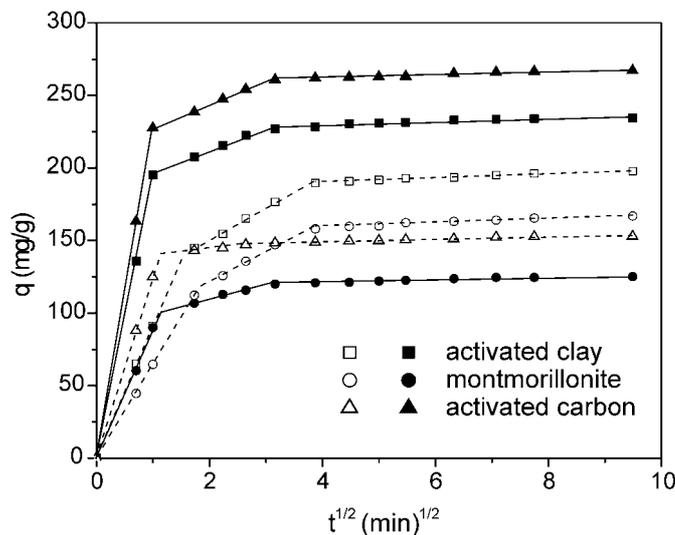


Figure 7. Test of intraparticle diffusion model for the adsorption of basic dyes on three adsorbents. (Filled for BG5 and open for BV10.)

found that q_e increases sharply with C_e at lower dye concentrations and then gradually levels off. The adsorption isotherm reveals the adsorption capacity of an adsorbent for dye adsorption at the plateau of the isotherm.

Adsorption isotherms are important to describe how adsorbates will interact with adsorbents and so are critical for design purposes. Therefore, the correlation of equilibrium data using an equation is essential to practical adsorption operation. Three isotherm equations were adopted in this study.

1. Langmuir isotherm

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_m}\right) + \left(\frac{1}{q_m}\right) C_e \tag{6}$$

where q_m is the amount of dyes adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage, K_L is the Langmuir constant.

2. Freundlich equation

$$\ln q_e = \ln K_F + n \ln C_e \tag{7}$$

where n and K_F are constants for a given adsorbate–adsorbent system at a fixed temperature.



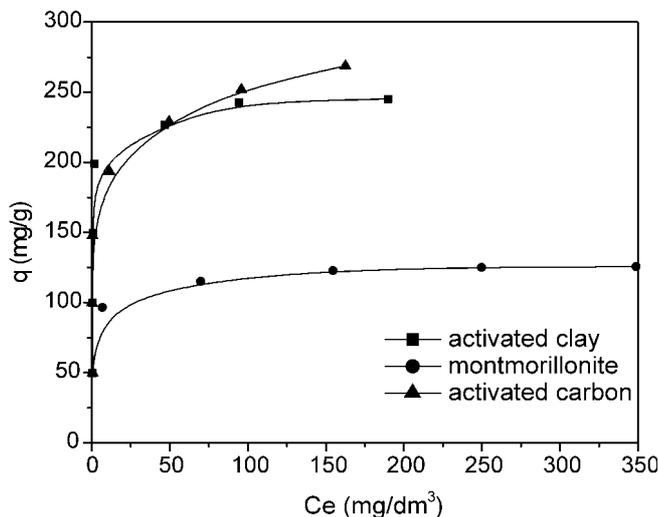


Figure 8. Adsorption isotherms of BG5 at 25°C on three adsorbents.

- Another useful improved model for the isotherms of dye is the following Langmuir–Freundlich equation:^[27]

$$C_e^n q_e = \left(\frac{1}{K_{LF} q_m} \right) + \left(\frac{1}{q_m} \right) C_e^n \quad (8)$$

where K_{LF} is the adsorption constant for this equation.

For the first two equations, the parameters can be obtained by plotting either (C_e/q_e) vs. C_e or $\ln q_e$ vs. $\ln C_e$. For the third equation, a minimization method is used to determine the best values of the three parameters. The adsorption curves were applied to the above isotherm equations.

The isotherm constants and their correlation coefficients, r^2 , for Figs. 8 and 9 are listed in Table 2. It is seen that the linear fit is fairly good for both Freundlich and Langmuir–Freundlich equations, but not for the Langmuir equation under the conditions of the present study. This implies multilayer adsorption occurred for all the adsorptions of two basic dyes on the adsorbents.

Effect of Temperature

Figures 10 and 11 are the plots of the adsorption isotherms of BG5 and BV10, respectively, on the activated carbon at different temperatures. It is



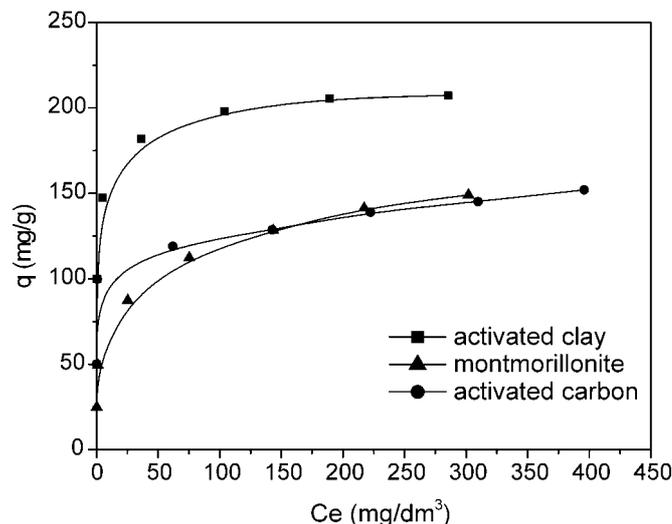


Figure 9. Adsorption isotherms of BV10 at 25°C on three adsorbents.

shown that the adsorption capacity increases with temperature. Similar results were observed for the other adsorbents.

The heat of adsorption (ΔH°) could be calculated from the temperature dependence of adsorption equilibrium constant, K .

$$\ln K = -\left(\frac{\Delta H^\circ}{RT}\right) + C \tag{9}$$

A linear plot of $\ln K$ against $1/T$ with a slope of $\Delta H^\circ/R$ is shown in Fig. 12. Other thermodynamic parameters, including the apparent free energy (ΔG°) and entropy (ΔS°), can be calculated by the following relations:

$$\Delta G^\circ = -RT \ln K \tag{10}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{11}$$

The values of ΔH° are determined to be 7.2 and 9.3 kJ/mol for BG5 and BV10 onto activated carbon, respectively. These small values of enthalpy change represent the no structure change occurred during the adsorption process. In general, the enthalpy change due to chemical adsorption (40–120 kJ/mol) is considerably larger than that due to physical adsorption (<40 kJ/mol). Hence, the adsorption of basic dyes BG5 and BV10 on activated carbon is probably due to the physical adsorption process for the described temperature range.



Table 2. Parameters of Langmuir, Freundlich, and Langmuir–Freundlich equations.

Model	Parameter	BG5			BV10		
		Activated clay	Montmorillonite	Activated carbon	Activated clay	Montmorillonite	Activated carbon
Langmuir	K_L	0.155	0.207	0.217	0.203	0.047	0.1
	q_m	271.3	127.6	272.0	216.5	158.3	149.0
	r^2	0.936	0.927	0.936	0.924	0.878	0.832
Freundlich	K_F	72.7	53.9	79.1	72.5	38.8	51.8
	n	0.278	0.155	0.272	0.218	0.238	0.186
	r^2	0.991	0.992	0.982	0.984	0.999	0.996
Langmuir–Freundlich	K_{LF}	0.259	0.434	0.341	0.403	0.154	0.352
	q_m	345.4	130.4	296.0	227.1	250.9	173.0
	n	0.5	0.71	0.64	0.65	0.39	0.46
	r^2	1.0	1.0	1.0	1.0	1.0	1.0

Note: K_L (dm^3/mg); q_m (mg/g); K_F ($\text{mg}/\text{g})(\text{dm}^3/\text{mg})^{1/n}$; K_{LF} ($\text{dm}^3/\text{mg})^{1/n}$.



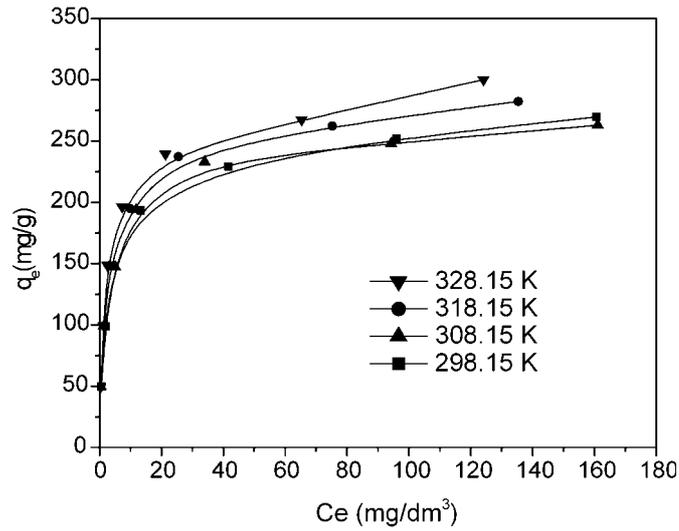


Figure 10. Adsorption isotherms of BG5 on activated carbon at different temperatures.

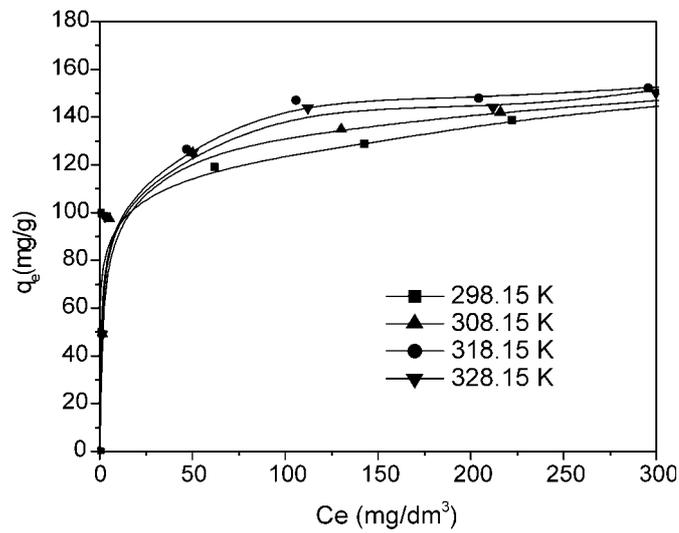


Figure 11. Adsorption isotherms of BV10 on activated carbon at different temperatures.



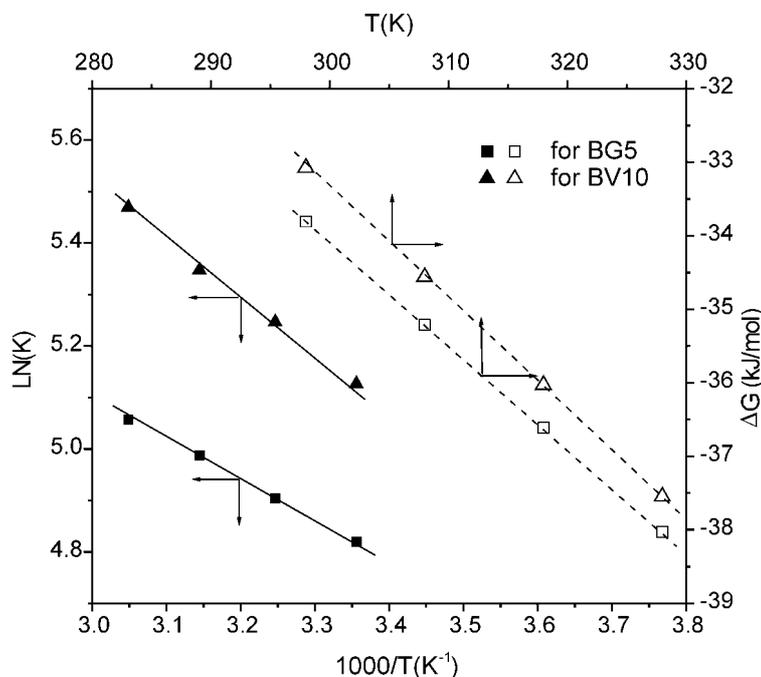


Figure 12. Determination of enthalpy of basic dyes adsorption on activated carbon and the plot of Gibbs free energy vs. temperature.

As expected, the negative value of ΔG° indicates that the adsorption process is spontaneous. The positive value of ΔH° reflect the endothermic nature of the process studied, which corresponds to the results of two simple processes: (a) the desorption of the molecules of solvent previously adsorbed, and (b) the adsorption of the molecules of dyes. Each molecule of dye has to displace more than one molecule of the solvent. The net result corresponds to the endothermic process.^[28] The positive value of ΔS° [see Eq. (11)] confirms that the adsorption of dyes on activated carbon is a combination of the two simple processes shown.

CONCLUSION

Two basic dyes, BG5 and BV10, with different molecular weights and structures were tested with three different adsorbents, activated clay, montmorillonite, and activated carbon. The dynamic data indicate that activated



carbon was suitable for BG5 but not BV10, primarily due to the molecular structure and montmorillonite was not good for either basic dye. The contact time process could be adequately fitted by the pseudo second-order equation for all the adsorption systems. The adsorption isotherms of dye could be well described by the Langmuir–Freundlich equation. The mean values of thermodynamic parameters were also obtained. The results indicate the adsorption is an endothermic process and an increased solution temperature would result in an increased adsorption capacity.

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