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Effect of Dye Nature on Its Adsorption from Aqueous Solutions onto Activated Carbon

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ABSTRACT

Liquid-phase adsorption of two dyes on activated carbon was measured in the 283–323 K temperature range. Higher capacity and faster kinetics of adsorption were obtained for a basic dye than for an acidic dye under comparable conditions, probably due to the different ionic natures of the dyes. The equilibrium data for acidic dye could be well described by the Freundlich equation, but the best-fit model for basic dye changed from the Langmuir to the Freundlich equations when the temperature was raised. In addition, the thermodynamic functions were determined. A plot of the fraction of adsorption against (time)$^{1/2}$ was adopted to describe the adsorption process. It was shown that for an acidic dye the amount of adsorbent used played an important role in the adsorption mechanism.

INTRODUCTION

Almost every industry, but mainly the textile industry, uses dyes to color its products. Many dyes are inert and nontoxic at the concentration discharged into the receiving waters; however, the color they impart is very undesirable to the water user. Also, some are harmful to the aquatic life in rivers where they have been discharged. The resulting wastewaters are highly toxic as some of them contain a large amount of metal complex dyes (e.g., Cr or Co complex). Therefore, color removal from textile wastewaters is a major environmental problem because of the difficulty of treating such waters by conventional chemical and biological methods

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TABLE 1
Chemical Nature of the Dyes Used in This Work

Name of dye	Classification	Color index	Molecular weight	Chemical nature	Ionic nature
Naphthol green B	Acid Green 1 (AG1)	10020	878.4	Nitroso	Anionic
Rhodamine B	Basic Violet 10 (BV10)	45170	479.0	Xanthene	Cationic

(1–3). Liquid-phase adsorption has been shown to be an effective method for color removal from aqueous streams (1–26), and activated carbon is the most widely used adsorbent for this process because it has a good adsorption capacity (12–26).

The two dyes used in this work are listed in Table 1. In general, dye compounds can be classified as basic, acidic, and other. While basic dyes possess cationic properties originating from positively charged nitrogen or sulfur atoms, acidic and other dyes possess an anionic nature due to negatively charged sulfonate groups (27). It may be noted that basic dyes with positive charges are so named because they have an affinity to basic textile materials with net negative charges, while acidic dyes with negative charges are so named because they have an affinity to acidic textile materials with positive charges.

Many studies on the adsorption of dyes onto activated carbon have been reported by McKay and coworkers (12–26). However, the effect of dye nature on its adsorption on activated carbon has not been fully clarified. The aim of this study is to compare activated carbon adsorption of one basic dye (Rhodamine B) and one acidic dye (Naphthol Green B) from aqueous solutions, including the equilibrium and kinetic behaviors. The effect of temperature on dye adsorption was examined, and the thermodynamic data were also evaluated.

EXPERIMENTAL

Materials

The chemical nature of the dyes used are listed in Table 1. The dyes came from Merck and were used without further purification. Powdered activated carbon (PAC) was also supplied by Merck and was used as received. According to the manufacturer's catalog, the particle size was less than 50 μm for a fraction greater than 99.5%, and the bulk density was about 280 kg/m^3. The BET surface area, pore volume, and average pore diameter were measured to be 13.2 m^2/g, 3.9×10^{-5} m^3/kg, and 11.8 nm, respectively, by Micromeritics ASAP 2000 (USA) in our laboratory. Aqueous solutions were prepared by dissolving the dyes in deionized water to the required concentrations. The deionized water employed in this work was produced by the Millipore Milli-Q Water System.

Procedure

In equilibrium experiments, a fixed amount of PAC (0.1–1 g) and 100 cm^3 of an aqueous solution were placed in a 250-cm^3 glass-stoppered flask and shaken at 130 rpm for 5 days using a thermostated shaker bath (Firstek Model B603, Taiwan). Preliminary experiments had shown that the adsorption studied was complete after 3 days. After filtration with glass fiber, the concentration of dyes in the aqueous solution was analyzed using a Hitachi UV/visible spectrophotometer (Model U-2000) at each suitable wavelength. Each experiment was duplicated under identical conditions.

The contact-time experiments were made in a batch Pyrex glass vessel as reported earlier (28). In each run an aqueous solution (1 dm^3) was first poured into the vessel and the timing was started upon the addition of PAC. The solution was mixed at 400 rpm using a Cole-Parmer Servodyne agitator with six blades and a flat-bladed impeller. At preset time intervals a sample (10 cm^3) was taken and immediately filtered. The concentrations of dyes in the aqueous solutions were analyzed as described above.

RESULTS AND DISCUSSION

Equilibrium Adsorption

Figures 1 and 2 show adsorption isotherms, that is, the relationships between the amount of dyes adsorbed per unit mass of PAC (q_e) and their final concentrations in the aqueous solutions (C_e), at different temperatures. It was found that the adsorption capacity, defined as the amount adsorbed at the plateau of the isotherm, for basic dye BV10 is greater than for acidic dye AG1 under comparable conditions. The present results are essentially similar to those observed for the adsorption of dyes by other adsorbents such as natural clay, wood, bagasse pith, and maize cob (2–4, 10, 14).

It is generally accepted that the capacity for activated carbon adsorption is higher when the adsorbate has a higher molar mass or a smaller solubility in water (29). This is not completely the case here since dye AG1 has a higher molar mass but a smaller water solubility than BV10. On a PAC

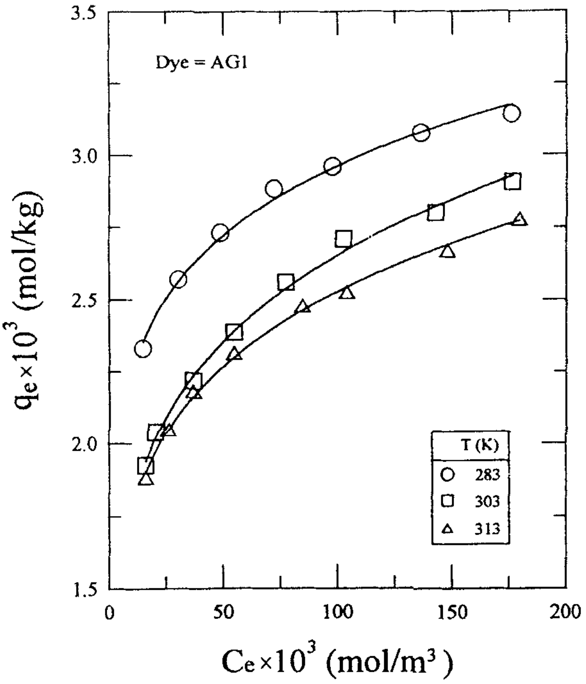

FIG. 1 Adsorption isotherms for dye AG1 on PAC at different temperatures.

surface there exist many conjugated π-bonds which are nonlocalized and highly active (30). After activation, a number of oxygen-containing functional groups exist in the crystal lattice of the surface, mainly the electron-acceptors (e.g., carbonyl and carboxyl). It is thus probable that electrostatic interaction occurs between the electron-acceptor groups on the PAC surface and the positive charges on basic dye compounds. Accordingly, the capacity should be greater for BV10 than for AG1 (27). This is in good agreement with the present findings.

It follows from Figs. 1 and 2 that the effect of temperature on adsorption capacity increases with temperature for both dyes in the 283–323 K temperature range. This suggests that the number of active sites available for adsorption increases with temperature. The increase in uptake of dyes with temperature may also be a result of the enhanced rate of intraparticle diffusion of adsorbates because the diffusion is endothermic (31, 32). The net increase, however, depends on the nature of the dyes (31). As clearly

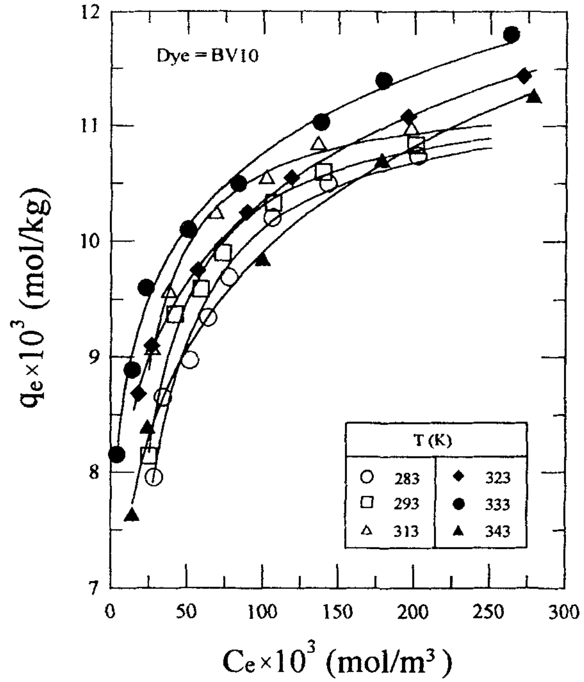

FIG. 2 Adsorption isotherms for dye BV10 on PAC at different temperatures.

shown in Fig. 2, however, the capacity for dye BV10 decreases when the temperature is raised beyond 333 K. Figure 3 also shows that at a fixed C_e, a maximum value of q_e is obtained around 330 K. This indicates that there may exist different molecular orientations or configurations for adsorption in contrast to the case of lower temperatures. The reverse of adsorption capacity due to a temperature increase has also been reported in other activated carbon adsorption systems (29).

Adsorption isotherms are important to describe how adsorbates will interact with adsorbents and so are critical in optimizing the use of PAC as an adsorbent. Thus, the correlation of equilibrium data using either a theoretical or empirical equation is essential to practical adsorption operation. Two isotherm equations were tried in the present study.

(1) Langmuir equation

$$C_e/q_e = (1/K_L q_{mon}) + (1/q_{mon})C_e \qquad (1)$$

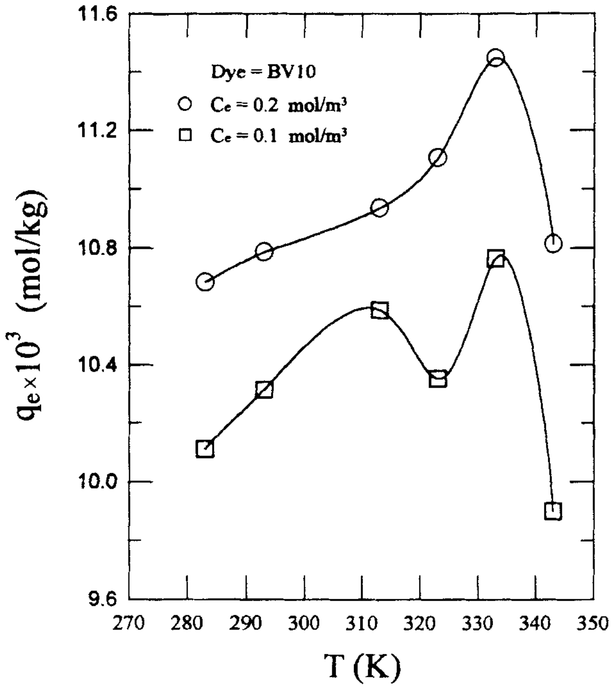

FIG. 3 Relationship between q_e and temperature at fixed C_e values for dye BV10.

where q_{mon} is the amount of dyes adsorbed per unit mass of PAC corresponding to complete monolayer coverage. K_L is the Langmuir constant.

(2) Freundlich equation

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{2}$$

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

The parameters in Langmuir and Freundlich equations can be determined from linear plots of either (C_e/q_e) vs C_e or $\ln q_e$ vs $\ln C_e$. Table 2 list the results obtained at different temperatures, together with correlation coefficients. It is seen that the linear fit is fairly good ($r > 0.986$) for both dyes under the concentration ranges studied. It should be noted that the better-fit equation for dye BV10 changes from Langmuir to Freundlich

TABLE 2
Parameters in Langmuir and Freundlich Equations at Different Temperatures[a]

		Langmuir			Freundlich		
Dye	T (K)	q_{mon}	K_{L}	r (—)	n	K_{F}	r (—)
AG1	283				8.22	3.92×10^{-3}	0.994
AG1	303				5.78	3.96×10^{-3}	0.996
AG1	313				6.37	3.63×10^{-3}	0.997
BV10	283	1.13×10^{-2}	82.1	0.986			
BV10	293	1.13×10^{-2}	104.6	0.986			
BV10	313	1.13×10^{-2}	147.7	0.994			
BV10	323				9.86	1.31×10^{-3}	0.997
BV10	333				11.3	1.32×10^{-3}	0.992
BV10	343				7.85	1.33×10^{-3}	0.995

[a] Units: q_{mon} (mol/kg), K_{L} ($\mathrm{m^3/mol}$), and K_{F} $(\mathrm{mol/m^3})^n(\mathrm{mol/kg})$.

while the temperature is rising. It is well known that the Langmuir equation is intended for a homogeneous surface. A good fit of this equation reflects monolayer adsorption. On the other hand, a good representation of the Freundlich equation, which is suitable for a highly heterogeneous surface, probably indicates multilayer adsorption.

Determination of Apparent Thermodynamic Functions

If the adsorption data can be well fit by the Langmuir equation, the isosteric enthalpy of adsorption, $\Delta H°$, the enthalpy of adsorption at a fixed coverage, θ ($= q_e/q_{\mathrm{mon}}$) could be determined from the temperature dependence of K_{L} (31).

$$(\partial \ln K_{\mathrm{L}}/\partial T)_\theta = -(\partial \ln C_e/\partial T)_\theta = \Delta H°/RT^2 \qquad (3)$$

A linear plot of $\ln K_{\mathrm{L}}$ against $1/T$ with a slope of $\Delta H°/R$ is shown in Fig. 4. Other thermodynamic functions, including the apparent free energy ($\Delta G°$) and entropy ($\Delta S°$), can be calculated by the following relations (31, 33):

$$\Delta G° = -RT \ln K_{\mathrm{L}} \qquad (4)$$

$$\Delta S° = (\Delta H° - \Delta G°)/T \qquad (5)$$

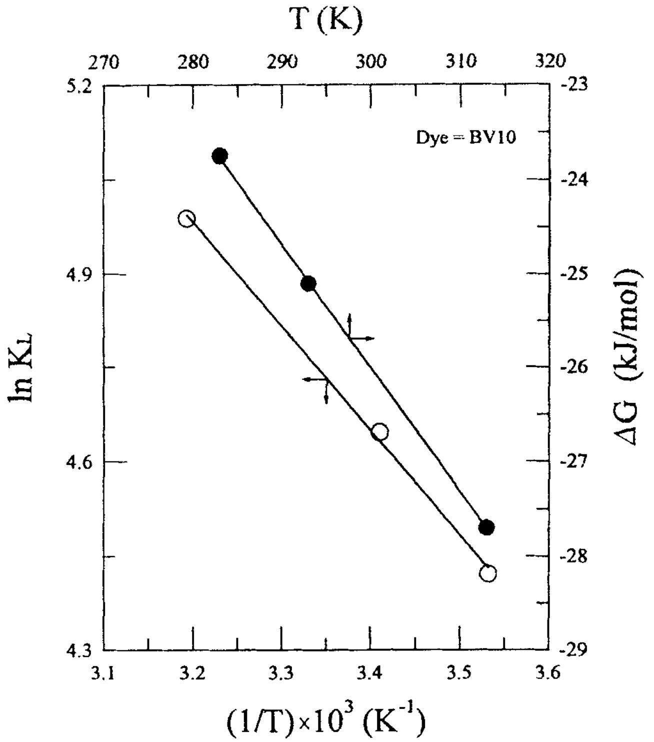

FIG. 4 Determination of the enthalpy of adsorption by two different ways.

It is worth noting that K_L in Eq. (4) should be used in molar units, dm^3/mol.

Another way to obtain thermodynamic functions based on Langmuir parameters is given by (29, 32)

$$\Delta G^\circ = -RT\ln(K_L q_{mon}/V_p) \tag{6}$$

$$\Delta S^\circ = -\{\partial(\Delta G^\circ)/\partial T\} \tag{7}$$

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \tag{8}$$

where V_p is the pore volume of the adsorbent. Figure 4 also shows these data.

The average values of $\Delta H°$ are determined to be 13.8 and 13.4 kJ/mol by Eqs. (3) and (8), respectively, and the mean values of $\Delta S°$ are 143.0 and 131.4 J/mol·K by Eqs. (5) and (7), respectively. Close agreement is apparent. In general, the enthalpy change due to chemical adsorption (40–120 kJ/mol) is considerably larger than that due to physical adsorption (below 40 kJ/mol) (32). Hence, the adsorption of basic dye BV10 on PAC is probably due to physical adsorption for the described temperature ranges.

As expected, the negative value of $\Delta G°$ indicates that the adsorption process is spontaneous. The positive value of $\Delta H°$ can be understood because the net process studied must correspond 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 an endothermic process (33). The positive value of

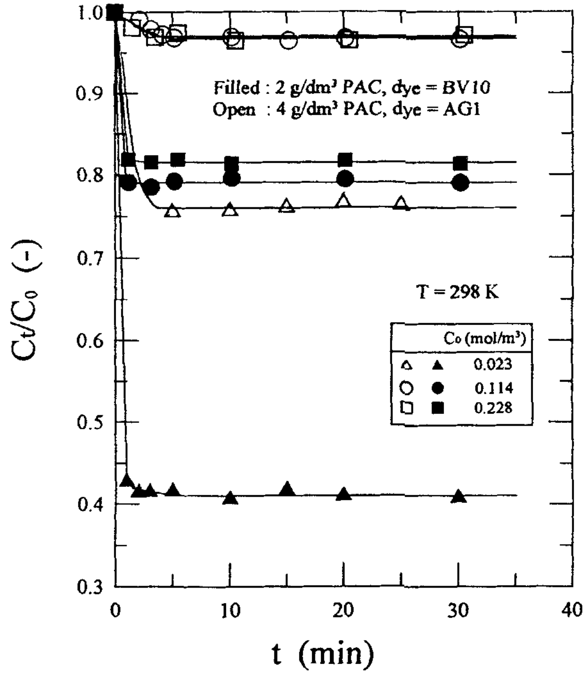

FIG. 5 Rate of dye adsorption on PAC at different initial dye concentrations.

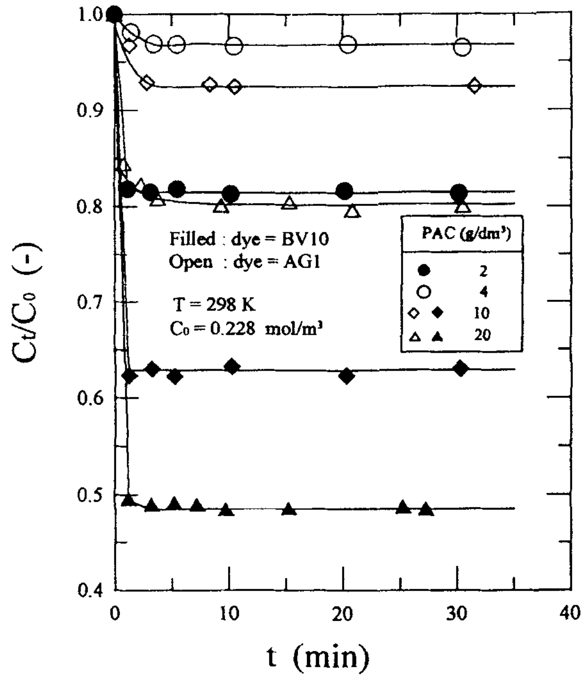

FIG. 6 Rate of dye adsorption on PAC at different amounts of PAC used.

ΔS° confirms that the adsorption of dye on PAC is a combination of the two above simple processes.

Adsorption Rates

In this work, time dependence of the adsorption process was obtained by batch contact-time experiments (Figs. 5–7). As in the case of adsorption capacity, it is seen that the adsorption is faster for BV10 than for AG1 under comparable conditions, which may be also due to strong electrostatic interaction between the basic dye and PAC. As expected, the dimensionless aqueous concentration (C_t/C_0) decreases more quickly at lower initial dye concentrations and with greater amounts of PAC used. Nevertheless, the value of (C_t/C_0) reduces more quickly at higher temperature for basic dye BV10, but that is reversed for acidic dye AG1.

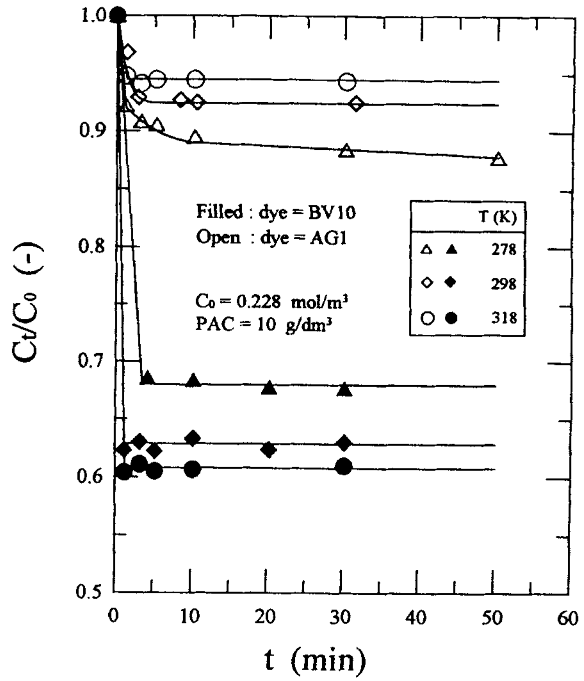

FIG. 7 Rate of dye adsorption on PAC at different temperatures.

The adsorption mechanism can be simply determined by plotting the fraction of adsorption Y against the normalized time $t^{1/2}$ (6–9, 16, 34, 35), where $Y = (q_t/q_e) = (C_0 - C_t)/(C_0 - C_e)$. Figures 8–10 show the results. In general, such a plot can be classified into three portions, and the positions of transition depend on adsorbate concentration and the type of adsorbate. The first, sharper portion is the external surface adsorption stage (8) or instantaneous adsorption stage (9). The second, gradual, linear portion is the gradual adsorption stage (9). The third portion is the final equilibrium stage (9, 16). In this model the spherical particles of adsorbent are considered as being surrounded by a boundary layer film through which the adsorbates must diffuse prior to external adsorption on the adsorbent surface, and this step is responsible for the first section. The second section of the plots is attributed to intraparticle diffusion being predominant in the rate-controlling step. As the bulk adsorbate concentra-

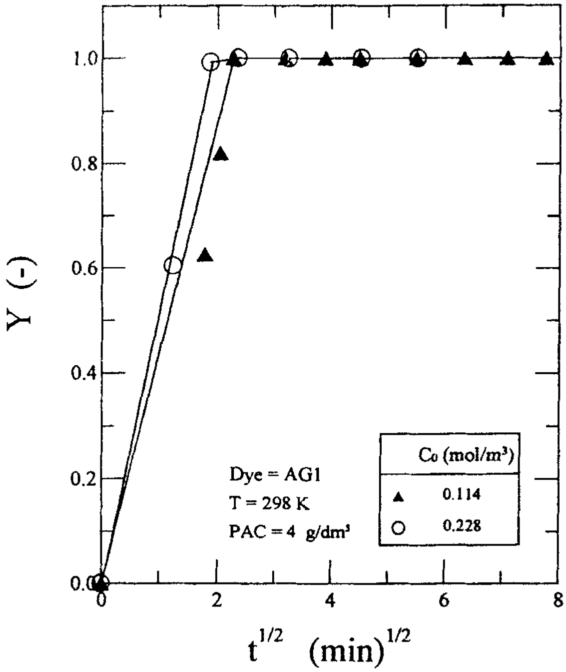

FIG. 8 Time dependence of the fraction of adsorption on PAC at different initial dye concentrations.

tion and the surface adsorbate concentration start to decrease, the third section of the plots is attributed to a decrease in the rate of diffusion.

Nevertheless, it follows from Figs. 8–10 that, two- or three-stage linear sections are observed, depending on the experimental conditions. Two-stage plots are obtained for the basic dye (not shown) and for the acid dye when the amount of PAC used is less than 4 g/dm^3. For BV10, the second gradual adsorption stage vanishes because of the electrostatic interaction between dye molecules and PAC. In the case of dye AG1, it is possibly due to the larger difference of dye concentration between the bulk aqueous solution and on PAC at a smaller dose of PAC, making the diffusion faster. Temperature and initial dye concentration have no effect on the general shape of such types of plots under the conditions studied.

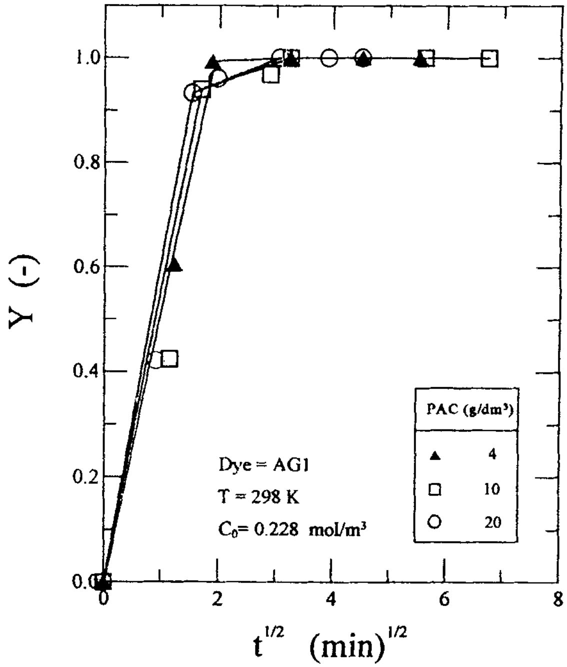

FIG. 9 Time dependence of the fraction of adsorption on PAC at different amounts of PAC used.

Alexander et al. (6) studied the adsorption of dyes on silica and also found three stages in equivalent plots. However, the shape was different, with an initial curved portion, a linear section, and a final curved portion. A linear plot of Y vs $t^{1/2}$ has been reported by Ruthven (36) on a theoretical basis. For batch adsorption of solutes on spherical particles, he indicated that for $Y < 0.3$ the solution of diffusion equations based on Fick's second law can be reduced to

$$Y \approx (2A/V)\,(D_p t/\pi)^{1/2} \tag{9}$$

where A/V is the ratio of the external area to the particle volume and D_p is the intraparticle diffusivity. In the case of a high fraction of adsorption, however, the linear relationship is merely an empirical observations (9, 16).

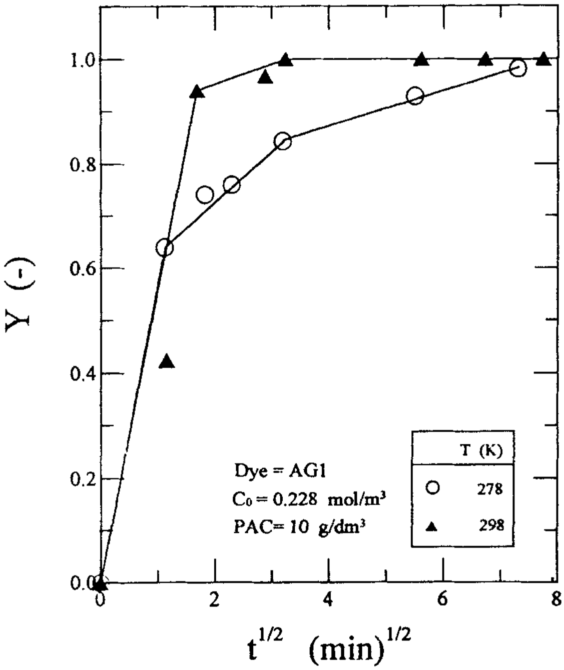

FIG. 10 Time dependence of the fraction of adsorption on PAC at different temperatures.

CONCLUSIONS

Equilibrium and kinetic studies on the adsorption of one acidic dye AG1 and one basic dye BV10 from dilute aqueous solutions on PAC have been carried out in the 283–323 K temperature range. The basic dye has a higher capacity and rate for PAC adsorption than the acidic dye under comparable conditions, which probably results from electrostatic interaction between the electron-acceptor groups on the PAC surface and the positive charges on the basic dye molecules. The Freundlich equation gives a good representation for acidic dye, but the better-fit equation for basic dye changed from Langmuir to Freundlich with rising temperature. The mean values of $\Delta H°$ and $\Delta S°$ of adsorption for the basic dye are 13.6 kJ/mol and 137.2 J/mol·K, respectively. Positive $\Delta H°$ and $\Delta S°$ values confirm that the adsorption of dye on PAC is a combination of two simple processes: (a) desorption of the molecules of solvent previously adsorbed and (b) adsorption of the molecules of dyes. Plots of the fraction of adsorption against $t^{1/2}$ show three-stage linear sections for AG1 when the amount of PAC used was greater than 10 g/dm^3; otherwise, two-stage plots are obtained, indicating the lack of a gradual adsorption stage.

NOTATION

C_e	equilibrium dye concentration in the aqueous solution (mol/m^3)
C_t	dye concentration in the aqueous solution at time t (mol/m^3)
C_0	initial dye concentration in the aqueous solution (mol/m^3)
ΔG°	standard Gibbs free energy (kJ/mol)
ΔH°	isosteric enthalpy of adsorption (kJ/mol)
K_F	parameter of Freundlich equation (mol/kg)(mol/m^3)^n
K_L	parameter of Langmuir equation (m^3/mol)
n	parameter of Freundlich equation (—)
q_e	equilibrium amount adsorbed on PAC (mol/kg)
q_{mon}	amount adsorbed corresponding complete coverage (mol/kg)
q_t	amount adsorbed on PAC at time t (mol/kg)
r	correlation coefficient (—)
R	universal gas constant (J/mol·K)
ΔS°	standard entropy change (J/mol·K)
t	time (min)
T	absolute temperature (K)
Y	fraction of dye adsorption (—)

Greek Letter

θ	fractional coverage (—)

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