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Elucidation of Controlling Steps of Reactive Dye Adsorption on Activated Carbon

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In this work, the rate-limiting steps of reactive dye adsorption onto FS-400 activated carbon were elucidated through the investigation of adsorption kinetics. These studies initially revealed that only 20% of the available adsorption capacity was achieved during the first 6 h of mixing. Kinetic profiles showed that the adsorption process was mainly controlled by external diffusion during the first 30 min of the reaction, after which internal diffusion controlled the process. The interruption test method identified the rate-limiting steps; the results showed that sorption of reactive dyes onto FS-400 was mainly controlled by internal diffusion. Furthermore, the external and internal diffusion coefficients and the desorption rate decreased after the interruption period. The same parameters increased when the solution temperature was raised. The thermodynamic parameters studied showed that the adsorption of reactive dyes onto activated carbon was endothermic and is mainly controlled by internal diffusion with a minor effect of external diffusion.

Introduction

Although equilibrium sorption studies are important in determining the effectiveness of adsorption, it is necessary to identify the types of adsorption mechanisms in a given system. To a large extent, the nature of the adsorption mechanism could determine the method of contacting wastewater with a specific solid adsorbent. Reactive dyes, the type considered in this work, are known to have low adsorbability on a wide range of adsorbents.[1] In the continuous search for effective adsorbents, six commercial activated carbons were tested for their ability to remove this problematic class of dye from textile wastewaters.[2] Screening tests[2] revealed that two of these activated carbons showed a good potential for reactive dye adsorption. The effect of the surface chemistry on dye adsorption was further investigated by the authors.[3,4] Based on preliminary kinetic studies, FS-400, a commercial activated carbon, was kinetically effective for removing reactive dyes from solution. To gain a better understanding of the complex reactive dye–activated carbon system, the nature of the controlling mechanism should be elucidated.

A number of mechanisms are suggested to control the sorption rate of dye–adsorbent systems. These include[5] (a) molecular diffusion from the bulk solution to a film layer surrounding the adsorbent particle; (b) diffusion from the film to particle surface, "film diffusion"; (c) migration inside the adsorbent particle by "surface diffusion" or diffusion within liquid-filled pores, "pore diffusion"; (d) and uptake, which includes several ways of interaction such as chemisorption, physisorption, ion exchange, or complexation.[5]

Of the mechanisms mentioned above, film and pore diffusion are most likely to prevail during dye adsorption onto activated carbon. The majority of research investigating dye sorption kinetics depends on Fick's law to describe the mass-transfer rates involved. External or internal diffusion can be controlling depending, in some cases, on the way in which the activated carbon is contacted with the reactive dye solution. External diffusion is most effective within column adsorption processes, while intraparticle diffusion is dominant in nonflow systems where a longer contact time is available. Therefore, from a practical standpoint, it is important to characterize the rate-controlling steps for reactive dye adsorption. In most dye adsorption kinetic investigations, the adsorption reaction on the adsorbent surface is always neglected compared to other working mechanisms.[6] The high loading values of reactive dyes reported earlier[4] confirmed that FS-400, after detailed kinetic investigation, could be practically effective for removing reactive dyes.

In this work, the rate-limiting step of reactive dye adsorption onto FS-400 is determined. External and internal diffusion coefficients (K_f and D) together with the Biot number (B_N) are obtained from the adsorption kinetic results to identify the various sorption mechanisms. In addition, mathematical manipulation and the nature of the rate-limiting steps are further characterized experimentally by using the "interruption test" method. Thermodynamic analyses of the systems and the resulting parameters (ΔH and ΔS) are then used to further elucidate the rate-limiting steps during reactive dye adsorption.

Mathematical Modeling of Adsorption Kinetics

Over 25 models are reported in the literature, all attempting to describe quantitatively the kinetic behavior during the adsorption process. Each adsorption kinetic model has its own limitation and is derived according to certain initial conditions based on specific experimental and theoretical assumptions. A number of these models assume linear equilibrium isotherms, while fewer models assume the equilibrium isotherms to be nonlinear. The mathematical background of some models was deduced from nonflow batch studies and

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fixed-bed studies. Different particle shapes were also assumed in a number of these studies.[6] Because of geometrical consideration, a diffusion process, rather than a simple surface reaction, will mainly control the adsorption of higher mass adsorbates, like reactive dyes. Weber and co-workers[7] had extensively studied the mechanisms of mass transport within porous adsorbents. A wide range of adsorbates, including strong and weak electrolytes and nonelectrolytes, were chosen for this purpose. The main conclusion of these studies was that, although there is some effect due to film diffusion at the surface−solution boundary, diffusion inside pores is the rate-determining step for most cases of adsorption from solution onto activated carbon.[7] The majority of research on dye adsorption systems confirmed that only two mechanisms controlled dye adsorption: external and internal diffusion.[8]

External Diffusion. Mass transfer of the adsorbate to the adsorbent particle is governed by a number of relationships obtained mainly from diffusion and mass balance equations. Numerical solutions are usually required to solve such equations. However, at the early stages of adsorption (0 and 30 min), the adsorption system is assumed to be controlled by an external diffusion mechanism, where the external diffusion coefficient, k_f (cm·s^{-1}), is given by[9]

$$\ln \frac{C_t}{C_0} = -k_f \frac{A}{V} t \tag{1}$$

where C_0, C_t, A/V, and t are the initial dye concentration, concentration at time t, the external adsorption area to the total solution volume, and adsorption time, respectively. Therefore, k_f may be calculated by plotting ln-(C_t/C_0) against the adsorption time, t. This equation is widely used in modeling kinetic data obtained for adsorption of dyes onto a number of adsorbents.

Internal Diffusion (Pore and Surface Diffusion). The introduction of this definition in adsorption systems was first introduced by Weber and Morris in 1963.[10] The authors observed that adsorption data were well fitted by plotting C_t/C_0 or C_t versus $t^{1/2}$. They studied the phenomena of mass transport within porous carbon adsorbents. McKay and Poots[11] also observed that a fraction of dye adsorbed could be linearly related to the square root of time. A plot of the fraction of solute adsorbed against $t^{1/2}$ is generally used to estimate the "sorption rate" during adsorption reactions. The mathematical relationship between the concentration of adsorbed substance onto the solid surface C_s, or ($C_0 - C_t$), and $t^{1/2}$ has been deduced by considering the sorption mechanism being controlled by intraparticle diffusion in the sorbent.[10] Assuming constant diffusion through adsorbent pores, the relation between the amount adsorbed and the reaction time can be presented by[10−12]

$$q_t = K_{ads} t^{1/2} \tag{2}$$

Equation 2 is considered to be one of the most frequently used equations to estimate the adsorption rate.[12] It has been applied to a number of adsorption systems and resulted in a high degree of correlation. One of its advantages is that the relative adsorption rate constant, K_{ads} (mg·g^{-1}·h$^{-1/2}$), can be readily calculated. Although it does not have the conventional rate constant units,

K_{ads} can be conveniently used to quantitatively describe the kinetics in the adsorption systems.

Once the adsorbate molecules accumulate at the outer surface of the adsorbent, internal diffusion commences. In fact, it is highly possible that both external and internal diffusion occur simultaneously; however, only one mechanism will control the whole adsorption process. In some adsorption systems, however, both mechanisms are thought to be significant in controlling the process.[13] As mentioned earlier, the high complexity of the diffusion equations can be simplified in order to calculate the corresponding parameters. Pore and surface mass diffusion is governed by Fick's law,[14] but some adaptations are proposed using some simplifying hypotheses. Intraparticle diffusion, D, the sum of pore and surface diffusion, may simply be calculated from the following equation:[15]

$$\frac{q_t}{q_\infty} = -\left[\log\left(1 - \left(\frac{q_t}{q_\infty} \right)^2 \right) \right] = \frac{4\pi D t}{2.3 d^2} \tag{3}$$

where q_t and q_∞ are respectively the solute concentration in the solid at time t and at equilibrium and d is the mean particle diameter.

Intraparticle diffusion coefficients can be estimated from the above equation by plotting q_t/q_∞ (only values less than 0.6 are considered)[15] versus adsorption time, t. Equation 3 was originally derived to estimate the internal diffusion coefficients for phosphorus adsorption.[15] This equation was derived by assuming that the adsorption rate is independent of the stirring speed and external mass transfer is not the rate-limiting step. Throughout adsorption literature, many simple equations are reported to calculate the internal diffusion coefficients D from kinetic adsorption data.[16] However, the results may vary from model to model within an acceptable range of error.[8]

In this study, adsorption kinetics of reactive dyes on FS-400 will be analyzed to identify the rate-limiting step. The heterogeneous porous structure of FS-400 observed from the scanned electron micrographs, together with the complexity of the reactive dye−carbon system, suggests that any of the aforementioned mechanisms could be controlling.

Interruption Test Method

The use of the interruption test method, specifically for identifying the rate-limiting step of reactive dye adsorption systems, is not reported in the literature. However, this method was used in 1949[13] to distinguish between external and internal diffusion processes during ion adsorption. Few investigators reported using interruption tests for identifying rate-limiting steps in adsorption systems.[13] In this method, the adsorbent is removed from the adsorption solution at a specific time and then reintroduced to the same adsorption solution after a certain period of time. During the interruption time, the initially sorbed material has a sufficient time to diffuse inside the adsorbent structure. After the adsorption reaction is restarted using the same adsorbent, intraparticle diffusion will be the rate-limiting step if the carbon capacity has altered from that recorded originally. On the other hand, external diffusion will be rate-limiting if the adsorbent is estimated to have the same removal capacity after the interruption period. Therefore, the interruption test method, along with mathematical treatment and thermodynamic studies,

is considered to be a simple and practical technique for elucidating the rate-limiting steps during dye adsorption onto the solid surface.

The Biot Number

Once the external and internal diffusion coefficients are determined for a given adsorption system, the Biot number can then be estimated from the following equation:[17]

$$B_N = k_f d/D \qquad (4)$$

where k_f, d, and D are the external diffusion coefficient (cm·s^{-1}), particle diameter (cm), and the internal diffusion coefficients (cm^2·s^{-1}), respectively. Adsorption processes where the Biot number is greater than 100 are mainly controlled by internal diffusion mechanisms.[17]

Thermodynamics of Diffusion-Controlled Processes. Adsorption of organic solutes from an aqueous solution onto activated carbon is an exothermic process.[18] The exothermic nature of adsorption is mainly due to reduction in the total entropy (ΔS).[19] However, the diffusion process of organic solutes within porous adsorbents, like activated carbon and molecular sieves, is endothermic in nature.[10,16,20] Because the diffusion process is endothermic, then the rate of uptake of organic solutes by porous solids will often increase with increasing temperature. Thermodynamic properties of diffusion processes can be related by the familiar Arrhenius equation:[20]

$$K_{ads} = Ae^{-E_a/RT} \qquad (5)$$

where K_{ads} is the rate constant, which is initially calculated using eq 2, T is the system temperature (K), and R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}), while A is a temperature-independent frequency factor. E_a is the minimum amount of energy required to start the reaction, i.e., activation energy.

The linear form of the above equation is

$$\ln K_{ads} = \ln A - \frac{E_a}{RT} \qquad (6)$$

Accordingly, a linear relationship between $\ln K_{ads}$ and $1/T$ is anticipated for an intraparticle diffusion-controlled process with a slope of $-E_a/R$. For two temperatures, T_1 and T_2 ($T_2 > T_1$), eq 6 can also be used to estimate activation energies for reactive dye adsorption systems:[10]

$$E_a = \frac{RT_1T_2}{T_2 - T_1}\left(\ln \frac{K_{1ads}}{K_{2ads}}\right) \qquad (7)$$

The variation of dye uptake with temperature could be presented by the relationship between the equilibrium distribution coefficients ($K_c = q_e/C_e$), where q_e and C_e are the amounts adsorbed at equilibrium [mg of dye·(g of carbon)$^{-1}$] and the equilibrium concentration [mg of dye.(g of solution)$^{-1}$], respectively. Such a relationship can be expressed in the form of the van't Hoff equation:[9,21,22]

$$\ln K_c = \ln \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (8)$$

The entropy, ΔS, and enthalpy, ΔH, can be obtained for dye diffusion processes by plotting $\ln K_c$ vs $1/T$. The linearity between $\ln K_c$ and $1/T$ is an indication that the uptake of dye molecules by FS-400 is an endothermic process.[23] Once the entropy and enthalpy have been calculated, the energy of adsorption of the reactive dye system can be calculated from eq 9:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (9)$$

Materials and Experimental Procedures

Adsorbent and Dyes. Three reactive dyes were used in this study, namely, Remazol Reactive Black, Remazol Reactive Yellow, and Remazol Reactive Red. Activated carbon Filtrasorb 400 (FS-400) was used as a solid adsorbent for these dyes. The specifications of the carbon and dyes are reported elsewhere.[2-4] FS-400 was supplied from Chemviron Carbon Ltd., U.K. Granular activated carbon was sieved using a standard British sieve apparatus (Endecotts Ltd., London, U.K.). Dye samples were obtained from the manufacturer directly (Bayer, Frankfurt, Germany). The isothermal behavior of the reactive dyes studied was reported by the authors.[4]

Most activated carbons have a porous structure which contain, a large number of cavities, pores, and channels. FS-400 carbon texture was examined using scanning electron microscopy. The mesopore volume was also determined by using the N$_2$ adsorption method.[24] It was found to be 0.13 cm^3·g^{-1}, and this significant volume is essential for dye adsorption.[24] On the other hand, micropore volumes are geometrically too small to accommodate dye molecules. Based on the FS-400 specification, the nature of dye interaction could not be a simple organic reaction, but instead different diffusion mechanisms could give a better representation of the adsorption data. Surface affinity for dye adsorption was determined from the methylene blue values.[25] FS-400 showed a high methylene blue value, 533 mg of dye·(g of carbon)$^{-1}$; i.e., more than 50% of the carbon mass is reactive for dye removal.

Experimental Procedure. The experimental system chosen for studying the adsorption kinetics of reactive dyes on FS-400 was the batch reactor method (BRM). Specifications of the adsorption reactor are detailed elsewhere.[26] A total of 1700 mL of dye solution with a desired concentration was prepared and poured into the 2000 mL adsorption vessel. Accurately weighed carbon, of the desired particle size range, was added. A mechanical stirrer, held by an adjustable motor, was used to agitate the solution. All adsorption kinetic studies were conducted at the same agitation speed. The initial concentration was measured before adding the carbon. The effect of the adsorption solution temperature on the adsorption kinetics of dyes was studied by controlling the temperature using a water bath and ensuring that there were no dead volume areas or any adsorbent trapped in the vessel. At specific time intervals, 4 mL samples were removed, filtered, and analyzed. The analytical measurement procedure is described elsewhere.[2-4] The sampling procedure continued until equilibrium was attained. The concentration of adsorbate on the solid surface, q_e [mg of dye.(g of carbon)$^{-1}$], was calculated by the standard mass balance equations. No noticeable sorption was observed onto the adsorption vessel.

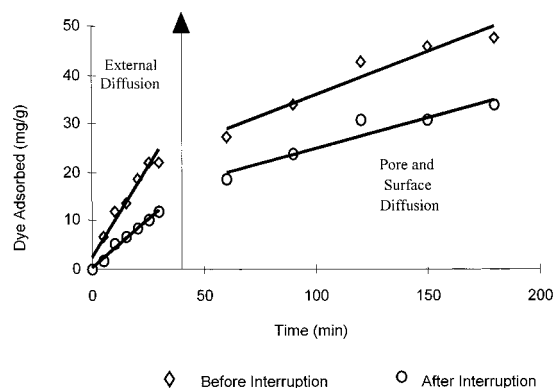**Figure 1.** Interruption test results of reactive yellow adsorption on FS-400. Experimental conditions: $C_0 = 85$ ppm, C_e(before test) $= 48$ ppm, C_e(after test) $= 57$ ppm, mass $= 1.0$ g, $T = 20$ °C, and $d_p = 600-710$ μm.
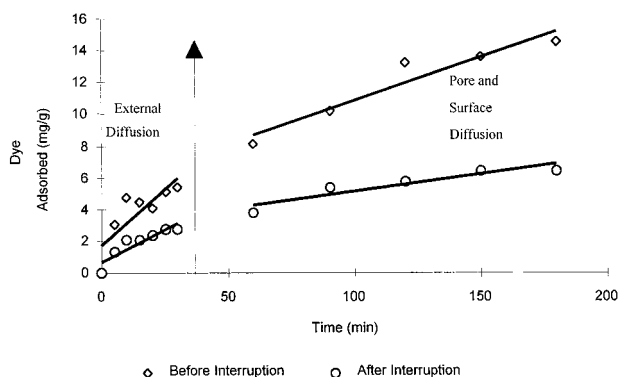

Figure 2. Interruption test results of reactive black adsorption on FS-400. Experimental variables: $C_0 = 100$ ppm, C_e(before test) $= 51$ ppm, C_e(after test) $= 79$ ppm, mass $= 5.0$ g, $T = 20$ °C, and $d_p = 710-850$ μm.

The interruption test was performed for dyes as follows: accurately weighed carbon beads of the desired particle size range were added to an adsorption solution of known concentration. The sampling procedure mentioned above was used. After 6 h of agitation, the adsorption reaction was terminated. The dye solution was decanted, and the remaining carbon beads were washed several times with distilled water. After 3 h of exposure to air, carbon beads were reintroduced to another dye solution which has the same concentration as that of the initial solution used in the first adsorption cycle. A similar sampling procedure was performed for the second adsorption cycle. By comparison of adsorption kinetics of the two runs, i.e., comparison of adsorption decay curves, the controlling mechanism can be determined.

Results and Discussion

Interruption Test Method. As mentioned earlier, the main aim of using the interruption test was to find a fast method for determining the rate-limiting step during dye adsorption onto activated carbon. Results of adsorption−interruption tests using reactive yellow, reactive black, and reactive red as the adsorbate are shown in Figures 1−3. The plots show that the sorption kinetic profiles of the three reactive dyes fall into two main regions: the external diffusion region (0−30 min) and the internal diffusion region (60−180 min). In fact, the discontinuity between the two regions, which is apparent in Figures 1−3, is an early indication of
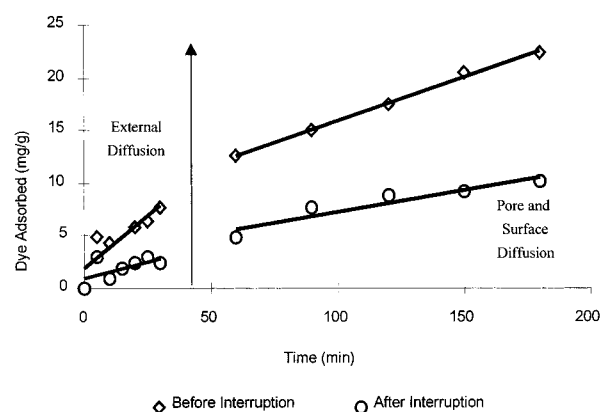

Figure 3. Interruption test results of reactive red adsorption on FS-400. Experimental variables: $C_0 = 100$ ppm, C_e(before test) $= 48$ ppm, C_e(before test) $= 72$ ppm, mass $= 3.50$ g, $T = 20$ °C, and $d_p = 300-500$ μm.

multimechanism sorption processes. As shown in these plots, all dye systems showed a decrease in adsorption kinetics after the interruption period, indicating the presence of a number of mechanisms in the second adsorption cycle. As noted, when different capacities in adsorption are obtained after interruption, intraparticle diffusion mechanisms are thought to be controlling. If external diffusion was the rate-limiting step, identical adsorption profiles should have been obtained, which is the case for phenol adsorption onto activated carbon after a specified interruption time.[13] This was not the case for the reactive dye−carbon systems investigated in this study.

A better linearity was obtained when the amount of dye adsorbed was plotted against $t^{1/2}$ rather than t. These plots are essential for determining the adsorption rate of dyes on FS-400. K_{ads} values, presented in Table 1, were calculated from the slope of the lines shown in Figure 4. At this early stage of analysis, eq 2 was applied to the adsorption data with t varying between 30 and 360 min. A typical $t^{1/2}$ plot has an s-shaped curve, while the center portion of the curve is expected to be linear. The rate of adsorption K_{ads} is usually estimated from the linear regression of this part. The slope of the linear portions of these curves, arbitrarily denoted as the removal rate, was calculated for each experiment via least-squares analysis.[13] Because the intraparticle diffusion is expected to be rate-limiting, the adsorption data were recalculated using the data obtained after 30 min of adsorption. The differences in K_{ads} values using both assumptions were found to be insignificant and are identical in some cases. These results are expected because the linear portion of the $t^{1/2}$ curve covered the majority of the adsorption data. In terms of sorption rates, FS-400 showed a lowered capacity after the interruption period (Table 1). Reactive yellow showed a high equilibrium adsorption capacity (730 mg·g^{-1})[4] and at the same time has a high kinetic uptake by FS-400 compared to the other two dyes. Although FS-400 showed a high equilibrium capacity for reactive dyes (200−750 mg·g^{-1}),[4] the sorption kinetic values were much smaller. This trend is usually expected for adsorption systems, and similar results were obtained for other adsorbents, although the magnitude of the reduction in some of these adsorbents was smaller than that recorded for activated carbon. For example, Lee et al.[9] reported an isotherm capacity of 58 mg·g^{-1} for a reactive dye using Hyacinth root and a sorption value of 10

Table 1. Sorption Kinetic Parameters (k_f, D, K_{ads}, and B_N) of Reactive Dyes

dye	external coefficients (cm·s^{-1})		intraparticle diffusion coefficients (cm^2·s^{-1})		Biot number		adsorption rate (mg·g^{-1}·h$^{-1/2}$)	
	k_f	$k_f{}^a$	D	D^a	B_N	$B_N{}^a$	K_{ads}	$K_{ads}{}^a$
yellow	4.42×10^{-2}	2.29×10^{-2}	3.50×10^{-7}	3.25×10^{-7}	> 100	> 100	28.73	21.82
black	1.00×10^{-2}	0.50×10^{-2}	6.73×10^{-7}	5.67×10^{-7}	> 100	> 100	8.30	4.00
red	7.02×10^{-3}	3.44×10^{-3}	1.31×10^{-7}	1.31×10^{-7}	> 100	> 100	12.66	6.70

^{a} After the interruption period.
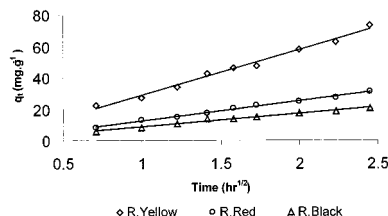
Figure 4. Cumulative removal rate versus square root of time for reactive dye−activated carbon systems.

Figure 5. Kinetic decay curves of reactive yellow sorption on FS-400. Experimental variables: $C_0 = 130$ ppm, mass = 1.00 g, $T = 20$ °C, and $d_p = 710-850$ μm.

mg·g^{-1}·h$^{-1/2}$ for the same dye−adsorbent system. On the other hand, FS-400 adsorbed 730 mg·g^{-1} of reactive yellow, while a relatively low value of 28 mg·g^{-1}·h$^{-1/2}$ was estimated for the corresponding sorption rate. The lower kinetic behavior of FS-400 is a strong indication of a multimechanism process.

Further inspection of the adsorption results reported in Table 1 shows that the amount of dyes adsorbed on the carbon was nearly halved for all of the dye−carbon systems considered. The reduction in the carbon adsorption rate and capacity after the interruption period did not follow the behavior obtained in other adsorption systems[10] where the dye molecules adsorbed in the first adsorption cycle are expected to create more available internal area for adsorption. This was not the case in this study where the carbon adsorption rate and capacity were reduced after the interruption period. The reduction in the carbon adsorption rate after the interruption time could be attributed to the slow diffusion of reactive dye molecules. Such a large molecular structure can hinder the movement of the adsorbate within the pores of carbon and accordingly reduce the sorption rates.

To gain a better understanding of the process, mathematical treatment was used to further represent the kinetic data. Kinetic data of dye adsorption on FS-400 before and after interruption were modeled to obtain the diffusion coefficients, adsorption rates, and Biot numbers by using eqs 1−4. The results are compiled in Table 1. As shown in this table, external diffusion coefficients of reactive dyes decreased after the interruption period. The same was also true for the internal diffusion coefficients for all of the dyes studied. It appeared that the intraparticle dye diffusivity was not affected to the same extent as external diffusion after the interruption period. It can be inferred that external diffusion is important during the initial stages of interaction. A 50% decrease in the external diffusion coefficient K_f values was found for the three dyes after interruption compared to a reduction in D values of between 0 and 15%. This high decrease in the external diffusion coefficient is attributed to the reduction in the external surface affinity for adsorption after interruption has taken place. Furthermore, the slight decrease in the internal diffusion coefficient values is attributed to the reduction in the internal surface affinity. It is noted that, if dye molecules did not diffuse inside the
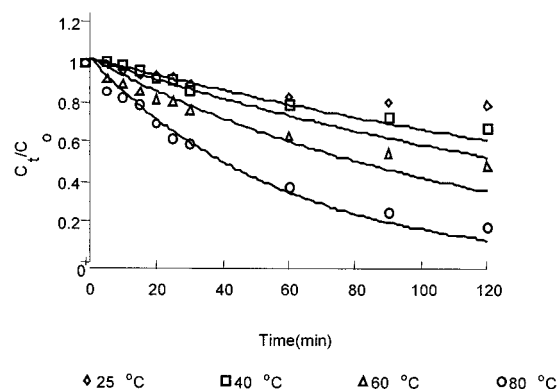
carbon structure during the interruption period, carbon is not likely to show any reactivity in the second adsorption cycle. In fact, the interruption test proved experimentally that dyes migrate further in the pore carbon structure after the abrupt termination of the adsorption process. Such a phenomenon is justified in highly porous adsorbents.

In this study, the Biot number (B_N) obtained for the various sorption systems was higher than 100 for all of these systems (Table 1), indicating that external diffusion has no physical significance for reactive dye adsorption onto FS-400.[27] The surface process was mainly controlled by intraparticle diffusion mechanisms. In theory, some factors are known to have an important impact on adsorbate transport in the adsorbent pore structure. These include the size and configuration of the adsorbate; high adsorbate affinity to adsorbent surfaces, which causes a decrease in the surface diffusion of the adsorbate; and pore construction and branching.[27] It is highly unlikely that dyes adsorbed in the first adsorption cycle have any effect on the carbon porosity. Therefore, the reduction in the carbon capacity for reactive dyes after the interruption period is mainly due to the reduction in the carbon affinity, and the adsorption process is mainly controlled by internal diffusion mechanisms.

Effect of Temperature on Adsorption Kinetics

The effect of dye solution temperature on sorption kinetics for reactive dyes is depicted in Figures 5 and 6. Concentration decay curves of reactive dyes at different temperatures were modeled using eq 1. k_f values reported in Table 2 were used to calculate the theoretical C_t/C_0 values. The results are shown in Figures 5 and 6. As shown in Figure 5, eq 1 predicts the sorption behavior only at early stages of adsorption (up to 30 min), after which the theoretical line deviates from experimental data. In Figure 6, a good fit to experimental data is obtained using eq 1. The failure of this
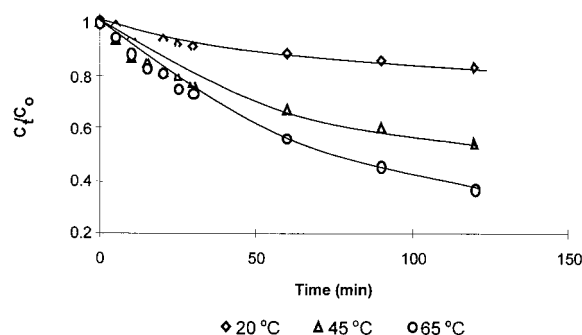
Figure 6. Kinetic decay curves of reactive black sorption on FS-400. Experimental variables: $C_0 = 100$ ppm, mass = 3.00 g, $T = 20$ °C, and $d_p = 710-850$ μm.

Table 2. Sorption Kinetic Parameters (k_f, D, K_{ads}, and B_N) of Reactive Dyes at Different Temperatures

dye	T (°C)	k_f (cm·s^{-1}) × 10^{-2}	D (cm^2·s^{-1}) × 10^{-7}	K_{ads} (mg·g^{-1}·h$^{-1/2}$)	B_N
yellow	25	1.78	4.61	36.00	>100
	40	3.30	5.32	54.00	>100
	60	6.04	16.30	79.00	>100
	80	13.79	24.10	119.00	>100
black	20	0.34	6.03	7.71	>100
	45	1.41	9.22	17.78	>100
	65	2.44	11.00	26.50	>100
	80	2.60	13.82	29.22	>100
red	20	1.60	12.1	10.68	>100
	45	3.10	9.90	14.20	>100
	65	4.13	11.34	18.55	>100
	85	7.33	13.82	23.82	>100

equation to predict the sorption behavior at the later stages of the adsorption process is mainly due to the involvement of intraparticle diffusion.

The effect of temperature on mass diffusivities, adsorption rates, and Biot number is summarized in Table 2. Unlike the sorption process, the diffusion process is endothermic. In Table 2, all sorption rates K_{ads} increased with temperature, which confirms the endothermic nature of the process; i.e., internal diffusion is the rate-limiting step during dye adsorption. It is worth mentioning that resistance to mass transfer is generally higher within the carbon compared to the external layers. Therefore, the calculated heat enthalpies mainly correspond to diffusion processes inside carbon pores. In fact, estimating the sorption parameters (K_{ads}, K_f, D, and B_N) at different temperatures is useful for identifying the rate-controlling steps. As shown in Table 2, external diffusivities (K_f) of the three dyes were more affected by temperature than internal diffusivities. For example, K_f values of reactive yellow increased 7.7 times between 25 and 85 °C, while D values increased 5.2 times. Similarly, K_f values of reactive black increased 7.6 times between 20 and 80 °C, while D values for this dye increased only 2.3 times for the same temperature range. It is noted that the solution temperature has less effect on reactive red kinetics. Results show that K_f values of the red dye increased by 4.6 times between 20 and 85 °C while D values increased only 1.1 times. It appears that dyes with a higher external diffusion coefficient tend to have higher kinetics compared to dyes with lower external diffusion coefficients. For example, reactive yellow has the highest external diffusion coefficients compared to the other two dyes and, consequently, has the highest sorption rate (Tables 1 and 2). Biot numbers higher than 100 were obtained for all dyes at all temperatures considered in this study, indicating

Table 3. Calculated Thermodynamic Parameters of Reactive Dye Adsorption onto FS-400 Carbon

dye	E_a (kJ·mol^{-1})	ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})	ΔG (kJ·mol^{-1})[a]
yellow	18.20	40.29	193	−17.19
black	19.33	52.55	225	−14.60
red	13.22	18.86	112	−14.52

[a] Calculated at room temperature.

an intraparticle diffusion-controlled process with a minor effect from external diffusion.[27]

Thermodynamic Parameters of Diffusion Processes

Because diffusion is an endothermic process, the sorption rate (K_{ads}) of reactive dyes increased by increasing the temperature, confirming intraparticle diffusion as the rate-limiting step.[10,16,20] Table 3 contains both the activation and enthalpy energies of dye sorption kinetics. Activation energy values, E_a, are close to those reported elsewhere.[10] These values are considered to be within the expected range of diffusional-controlled processes. The reported ΔH values calculated in this study are close to those reported for similar types of dyes.[9,28] The positive ΔH values indicate the endothermic nature of reactive dye adsorption. However, these values are relatively small, which is an indication of a diffusion-controlled process.[28] Negative ΔG values indicate that the sorption process of reactive dyes on FS-400 is spontaneous at room temperature. The lower ΔH value of reactive red compared to other dyes explains its low affinity to the carbon surface.[4] It should be mentioned that ΔH reported here is the heat evolved during sorption kinetics (heat evolved due to the diffusion process). ΔH for the whole adsorption reaction is usually negative, i.e., an exothermic process. Such values can be calculated by conducting full aqueous isotherms at different temperatures.[29] Practically, most wastewater is usually treated by activated carbon at low temperatures. Accordingly, the heat of adsorption reaction of reactive dyes was not considered in this study. Only the heat of sorption kinetics was considered in order to identify the sorption mechanisms.

It is generally expected that sorption processes (from both gas and liquid phases) have an exothermic nature because an overall reduction in the system entropy usually occurs.[7,18,19,29] It seems that adsorption in aqueous systems is different from that in gas systems, which may be endothermic or exothermic in nature.[18] The positive ΔH and ΔS reported here can be attributed to two simple processes:[29] (i) the exchange of the molecules of solvent (water) previously adsorbed and (ii) the adsorption of dye molecules. Each molecule of the dye has to displace more than one molecule of water. The net result corresponds to an endothermic process, i.e., positive ΔH and ΔS.

As was inferred earlier from interruption tests, intraparticle diffusion was the overwhelming step during adsorption of reactive dyes; furthermore, the internal diffusion process was further confirmed by the positive ΔH value. In fact, the validity of such relationships (eqs 6 and 8) strongly indicates that dye sorption kinetics was mainly controlled by intraparticle diffusion processes.[20] A positive ΔH value was reported for Direct Red sorption on Biogas sorbent. A positive ΔH value was attributed to the endothermic nature of dye adsorption.[21]

Conclusions

Although FS-400 activated carbon has an outstanding adsorption capacity for reactive dyes, it showed a moderate kinetic capacity. Only 20% of the available ultimate capacity was achieved during the first 6 h of mixing with a dye solution. Interruption test results showed that sorption of reactive dyes onto FS-400 was mainly controlled by internal diffusion, with only a minor effect from external diffusion. Furthermore, k_f, D, and K_{ads} of reactive dyes decreased after the interruption period for the adsorption systems considered in this study. k_f values were more affected than D values using this interruption. Sorption parameters (k_f, D, and K_{ads}) of reactive dyes all increased by increasing the solution temperature. It was observed that k_f values were more responsive to temperature than D values. The adsorption rate parameter, K_{ads}, was significantly increased at higher solution temperatures. The thermodynamic parameters (ΔH, ΔS, and ΔG) showed that sorption of reactive dyes onto FS-400 has an endothermic nature. Adsorption of reactive dyes onto FS-400 is a spontaneous process at room temperature.

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