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The Adsorption Kinetics of *Cethyltrimethylammonium Bromide* (CTAB) onto Powdered Active Carbon

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Abstract. This study investigates the adsorption kinetics of CTAB (cethyltrimethylammonium bromide), a cationic surfactant, onto PAC from aqueous solution with respect to the initial CTAB concentration at 20°C. The pseudo-first-order, second-order kinetic models and intraparticle diffusion model were used to describe the kinetic data and the rate constants were calculated. The rate parameter, k_i, of intraparticle diffusion, the rate parameter, k_2, of the pseudo-second-order and k_1, the rate parameter for the pseudo-first-order mechanism were compared. It was found that the pseudo-second-order adsorption mechanism is predominant and the overall rate of the CTAB adsorption process appears to be controlled by more than one step, namely both the external mass transfer and intraparticle diffusion mechanisms.

Keywords: adsorption kinetics, CTAB, powdered active carbon, pseudo-first order kinetics, pseudo-second order kinetics, intraparticle diffusion

1. Introduction

Adsorption of surfactants at the solid/liquid interface has been extensively studied during the last four decades. One reason for this interest is the importance of surfactants adsorption on solid surfaces in many industrial applications in order to improve efficiency and economy. Therefore, it is essential to understand the mechanism and kinetics of adsorption, because the studies of adsortion kinetics is ultimately a prerequisite for designing an adsorption column. The sorption of pollutants from aqueous solution plays an important role in wastewater treatment since it eliminates the need for huge sludge-handling processes. Well-designed sorption processes have high efficiency resulting in a high-quality effluent after treatment which can be recycled. The kinetics of surfactant adsorption is a fundamental problem of interfacial science playing a key role in various processes and phenomena, such as wetting, foaming and stabilization of liquid films (Ho and McKay, 1999; Juang et al., 2000).

The adsorption kinetics from surfactant solutions is comprehensively studied (Hutchison et al., 1999; Vlahovska et al., 1997). The study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and into

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the mechanism of sorption reactions due to the fact that as it was based on the process kinetics reaction mechanisms may be hypotezited. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants.

Activated carbon has been widely used in wastewater treatment to remove organic and inorganic pollutants (Ho and Chiang, 2001; Tseng et al., 2003; Meshko et al., 2001; Wu et al., 2001, 2002; Yang and Al-Duri, 2001; Chen and Lin, 2001; Chiang et al., 2000). Possessing high surface area, activated carbon frequently exhibits high removal efficiency for most dissolved compounds. The removal efficiency is influenced by the characteristics of the activated carbon, such as surface properties, area and chemical characteristics. In general, the characteristics of activated carbon are controlled by the manufacturing process. Depending on the nature of the raw materials, the nature of the activating agent and the conditions of the activation process, the properties of the activated carbon can be varied (Donati et al., 1994; Bradley and Rand, 1995). Therefore, PAC (powdered active carbon), a pure and carbon-based substance, was chosen as the adsorbent. The aim of the present study is to identify the adsorption kinetics of CTAB, a cationic surfactant, onto PAC from aqueous solution for a CTAB-active carbon system.

2. Material and Methods

In the study, as adsorbate, a cationic surfactant, CTAB (*cethyltrimethylammonium bromide*), which has a long hydrocarbon chain, was chosen. CTAB was crystallized three times with $CHCl_3$prior to use. A commercial PAC (powdered active carbon) with a BET surface area of 900 m^2/g, particle size of 150 μm (<80%) (Merck cat. no. 2184) was used as adsorbent.

2.1. Adsorption Kinetic Modelling

Batch adsorption experiments for the study of the adsorption kinetics were carried out in 100 mL; glass-stopperred, round-bottom flasks immersed in a thermostatic shaker bath at constant temperature, 20°C and pH 9.9, which were controlled during the sorption process. For this, 0.10 g of active carbon was mixed with 100 mL of the aqueous solutions of the various initial concentrations (30, 60, 90, 120, 150, 180, 240 and 300 mg/L) of CTAB. The flasks with its contents were then shaken for the different adsorption times at 20°C.

The concentration of CTAB in the supernatant solution was determined by using a double-beam UV spectrophotometer at 375 nm and in the presence of 0.02 mL of 0.1% picric acid in 0.002 M NaOH and 0.40 mL of 1,2-dichloroethane per 1.0 mL of the supernatant (Rosen and Goldsmith, 1972). It was found that the calibration curve was very reproducible and linear over the concentration range used in this study. The amount of the CTAB adsorbed was calculated from the concentrations in solution before and after adsorption. Blanks containing no CTAB were used for each series of experiments. Plots of the sorption capacity (mg/g) as a function of sorption time (0–120 min) for the eight different CTAB concentration are shown in Fig. 1.

2.1.1. Pseudo-First-Order Model. In order to investigate the mechanism of adsorption, the pseudo-first-order adsorption, the pseudo-second order adsorption and the intraparticle diffusion model were used to test kinetic experimental data.The pseudo-first order rate expressison of Lagergren is generally described by the following equation (Tseng et al., 2003; Chiou and Li, 2003; Jain and Sharma, 2002; Ho and McKay, 1998).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

where q_e and $q_t$are the amounts of CTAB (mg/g) adsorbed on the activated carbon at quilibrium, and at time t, respectively and k_1 is the rate constant (min^{-1}). Integrating and applying the boundary condition, $t = 0$ and $q_t = 0$ to $t = t$ and $q_e = q_t$ Eq. (1) takes the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

The rate k_1 was obtained from slope of the linear plots of $\log(q_e - q_t)$ against t. For various initial CTAB concentrations k_1 obtained for adsoprtion over the first 120 min are given in Table 1 along with the corresponding correlation coefficients.

2.1.2. Pseudo-Second-Order Model. The sorption data was also analysed in terms of a pseudo-second order mechanism, described by Ho and Chiang (2001), Tseng et al. (2003), Wu et al. (2002), Ho and McKay (1998, 2003).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where k_2 is the rate constant of pseudo-second order sorption (g/mgmin). Integrating and applying boundary

Table 1. The effect of initial concentration on CTAB adsorption parameters.

Initial CTAB conc.	Pseudo-first order model			Pseudo-second order model				
(C_0, mg/L)	$q_{e,1,\text{pre.}}$	r_1^2	k_1 (min^{-1})	$q_{e,2,\text{pre.}}$(mg/g)	k_2 (g/mg min)	h (mg/g min)	r_2^2	$q_{e,\text{exp}}$
30	7.24	0.815	0.0261	30.30	0.0681	62.50	0.9997	30.0
60	8.43	0.586	0.0130	62.50	0.0269	105.26	0,9998	60.5
90	15.13	0.708	0.0130	90.90	0.0195	161.29	0.9997	90.6
120	28.84	0.823	0.0374	120.6	0.0153	222.22	0.9997	120.0
150	30.90	0.805	0.0374	151.5	0.0136	312.50	0.9997	150.0
180	45.71	0.789	0.0261	181.8	0.00890	294.12	0.9997	179.8
240	67.61	0.856	0.0217	238.1	0.00551	312.50	0.9997	236.0
300	50.12	0.622	0.0130	285.7	0.00471	384.62	0.9998	287.5

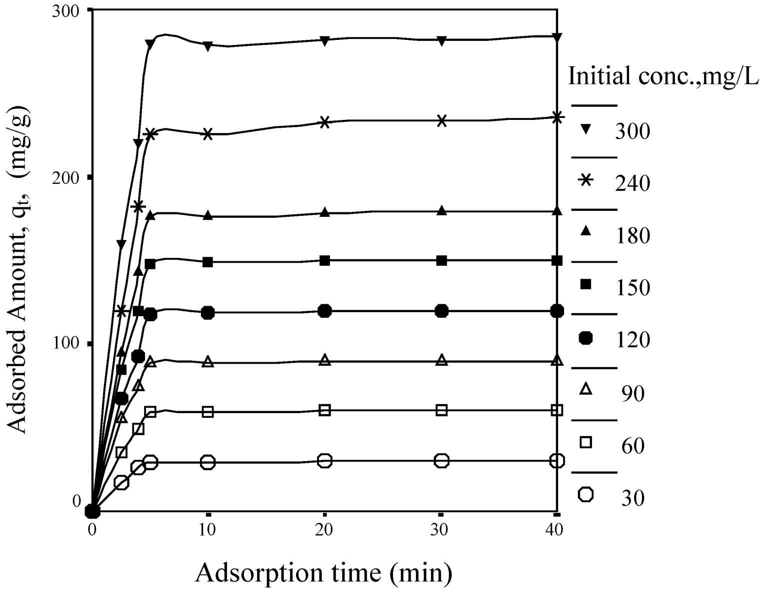

Figure 1. Amount of CTAB sorbed versus time for different initial CTAB concentrations (20°C, pH 9.9).

conditions $t = 0$ and $q_t = 0$ to $t = t$ and $q_e = q_t$ Eq. (3) becomes

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{4}$$

which has linear form of

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

If initial adsorption rate is

$$h = k_2 q_e^2 \tag{6}$$

then Eqs. (4) and (5) become

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \tag{7}$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{8}$$

If second-order kinetics is applicable, the plot of $\frac{t}{q_t}$ against t of Eq. (8) should give a linear relationship from which the constants q_e, h and k_2 can be determined.

The values of constants q_e, h and k_2 for pseudo-second order sorption have also been given in Table 1. As can be seen from Table 1, the correlation coefficient for second order kinetics at all CTAB concentrations was >0.9996. By comparing the pseudo-first order and pseudo-second order adsorption rate constants at different initial CTAB concentrations, it is seen that the second order model provides the best correlation of data.

2.1.3. Intaparticle Diffusion Model. It has also been demonstrated that PAC has a highly porous surface area. This type of adsorbent structure results in intraparticle diffusion being the rate limiting step. Intraparticle diffusion can be described by three consecutive steps.

(i) The transport of sorbate from bulk solution to outer surface of the sorbent by molecular diffusion, known as external (or) film diffusion.
(ii) Internal diffusion, the transport of sorbate from the particles surface into interior sites.
(iii) The sorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the sorption process will be controlled by the slowest, the rate limiting step. In adsorption systems where there is the possibility of intraparticle diffusion being the rate-limiting step, the intraparticle diffusion approach described by Weber and Morris is used. The rate constants, for intraparticle diffusion (k_i) are determined using equation given by Waber and Morris. This equation can be described as Jain and Sharma (2002), Basibuyuk and Forster (2003) and Sivaraj et al. (2001);

$$q_t = k_i t^{0.5} + c \tag{9}$$

where k_i and c is intraparticle diffusion rate constant (mg/gmin$^{0.5}$) under different initial concentration of CTAB and a constant, respectively. The k_i is the slope of straight-line portions of plot of q_t vs. $t^{0.5}$. These plots have generally the double nature, i.e. initial curve portions and final linear portions. This is explained by the fact that the initial curved portions are boundary layer diffusion effects. The final linear portions are a result of intraparticle diffusion effects. An extrapolation of the linear portions of the plots back to the axis yield intercepts (c) which are proportional to the extent of boundary layer thickness (Jain and Sharma, 2002).

2.1.4. Diffusion Coefficient. In this study, the pore diffusion coefficients, D, within the pores of adsorbents at various concentrations was determined using the following equation (Annadurai et al., 2000; Sun and Yang, 2003; Tseng et al., 1999):

$$t_{1/2} = \frac{0.030 r_0^2}{D} \tag{10}$$

where D, $t_{1/2}$ and r_0 represent the pore diffusion coefficient, the time for half-adsorption and the radius of the adsorbent particle, respectively (Table 3). In these calculations, it has been assumed that the solid phase consists of spherical particles having an average radius between the radii corresponding to upper and lower size fractions.

3. Results and Discussion

3.1. Effect of Initial CTAB Concentration

Figure 1 shows the effect of initial CTAB concentration on the adsorption kinetics of the CTAB at pH 9.9, 20°C. An increase in initial CTAB concentration leads to an increase in the adsorption capacity of CTAB on PAC. While initial CTAB concentration increase from 30 to 300 mg/L, the adsorption capacity of CTAB onto PAC changes from 30 to 287.5 mg/g. This indicates that the initial CTAB concentration plays an important role in the adsorption capacity of CTAB on PAC.

Figure 2 shows plots of $\log(q_e - q_t)$against t for the pseudo-first order equation for the sorption of CTAB. The correlation coefficients, r_1^2, the first-order rate parameters, k_1, and sorption capacity, $q_{e,1}$ are shown in Tables 1. The equilibrium sorption capacity increased from 7.24 to 50.12 mg g^{-1} when the initial concentration of CTAB increased from 30 to 300 mg/L, indicating that the CTAB removal is dependent on initial concentration. However, the values of the rate constant, k_1, were found to decrease from 0.0261 to 0.013 min^{-1} for an increase in the initial concentration from 30 to 90 mg/L. Then, for an increase in the initial concentration from 150 to 300 mg/L, values of the rate constant were found to decrease from 0.0261 to 0.0130 min^{-1}. The regression coefficients for first order model is rather low, namely, between 0.856 and 0.586. Therefore, first order model do not show good compliance with experimental data.

Figure 3 shows plots of t/q_t against $t$for the pseudo-second order equation for the sorption of CTAB. The correlation coefficients, r_2^2, and the pseudo-second order rate parameters, k_2, are shown and compared with r_1^2, r_i^2 and k_1, k_i values for the pseudo-first order reaction mechanism and intrapaticle model (Tables 1 and 2). The data show a good compliance with the pseudo second order equation and the regression coefficients for the linear plots were higher than 0.9996. The kinetics of CTAB sorption on PAC follows the pseudo-second order rate expression. The equilibrium sorption capacity, $q_{e,2}$, increased from 30.3 to 285.7 mg g^{-1}

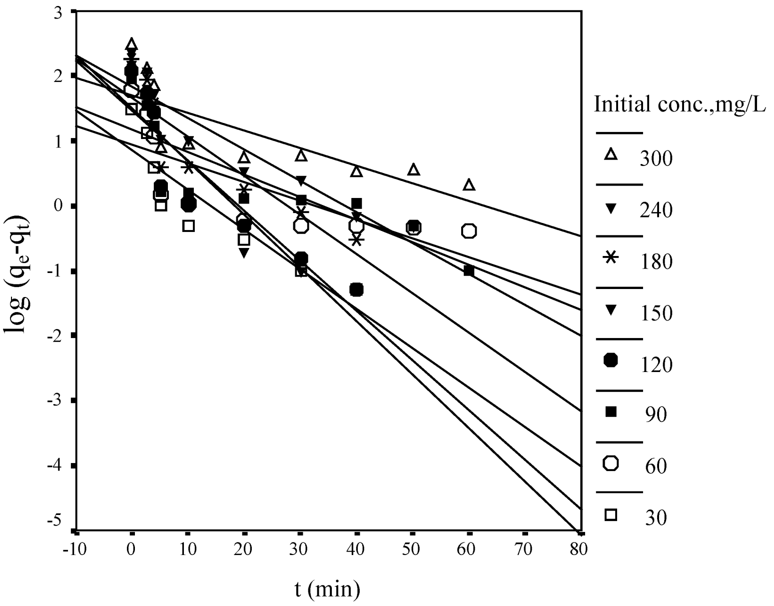

Figure 2. Pseudo-first order kinetics plot for adsorption of CTAB on PAC.

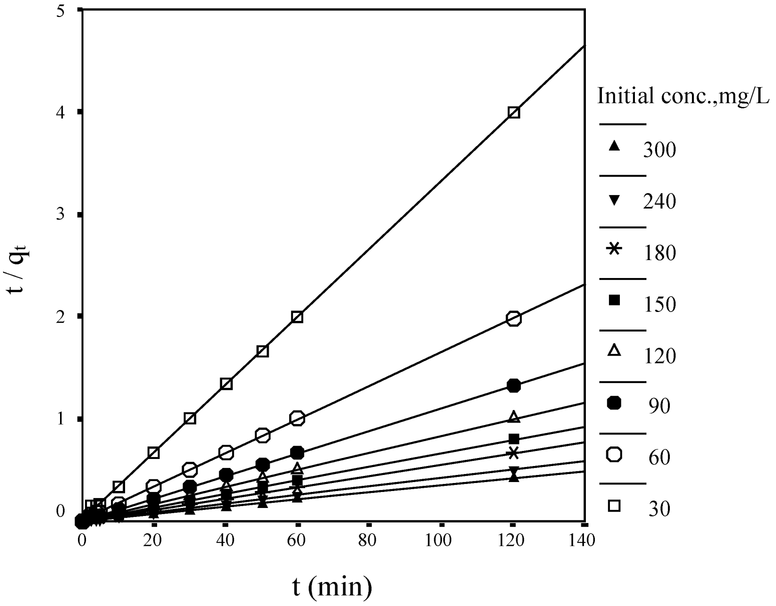

Figure 3. Pseudo-second order kinetics plot for adsorption of CTAB on PAC.

when the initial concentration of CTAB increased from 30 to 300 mg/L, indicating that the CTAB removal is dependent on initial concentration. The values of the rate constant, k_2, were found to decrease from 0.0681 to 0.00471 g/mgmin for an increase in the initial concentration from 30 to 300 mg/L. The value of the initial sorption rates, h, was determined by using the values of the intercepts of the straight lines plotted in Fig. 3. The initial sorption rate increases with a decrease in the initial CTAB concentrations. While the C_0 varies from 30 to 300 mg/L, as expected, h varies from 62.50 to 384.62 mg/gmin because the driving force of sorption increases. However, when $C_0 > 150$ mg/L is, h change in an abnormal order.

Table 2. The constants and values for Eqs. (11)–(13).

A_q (g/mg)	B_q (g/L)	A_h (g/mg)	B_h (gmin/L)	A_k2 (gmin/mg)	B_k2 (mg^2 min/g)
$3.37\ 10^{-4}$	$9.40 \cdot 10^{-1}$	$1.32 \cdot 10^{-3}$	0.385	91.04	$-2.29 \cdot 10^{3}$

The corresponding linear plots of the values of $q_{e,2}$, k_2 and h against C_0 were regressed to obtain expressions for these values in terms of the initial CTAB concentration with high correlation coefficients (Table 2). Therefore it is further considered that $q_{e,2}$, k_2 and h can be expressed as a function of C_0 for CTAB as follows:

$$q_{e,2} = \frac{C_0}{A_q C_0 + B_q} \quad r^2 = 0.9995 \tag{11}$$

$$h = \frac{C_0}{A_h C_0 + B_h} \quad r^2 = 0.9950 \tag{12}$$

$$k_2 = \frac{C_0}{A_{k_2} C_0 + B_{k_2}} \quad r^2 = 0.9940 \tag{13}$$

Substituting the values of $q_{e,2}$, k_2 and h from Table 1 into Eqs. (11)–(13), the empirical parameters in these equations were obtained. The values of A_q, B_q; A_{k2}, B_{k2}; A_h, B_h are given in Table 2.

Substituting the values of $q_{e,2}$ and h from Table 2 into Eqs. (11) and (12) and then into Eq. (8), the rate law for a pseudo-second order and the relationship of q_t, C_0 and t can be represented as follows:

$$\begin{aligned} q_t &= \frac{t}{\frac{1}{h} + \frac{t}{q_e}} = \frac{t}{\frac{1}{\left(\frac{C_o}{A_h C_o + B_h}\right)} + \frac{t}{\left(\frac{C_o}{A_q C_o + B_q}\right)}} \\ &= \frac{C_o t}{(A_h C_o + B_h) + t(A_q C_o + B_q)} \Rightarrow q_t \\ &= \frac{C_o t}{1.32.10^{-3} C_o + 0.385 + t(3.37.10^{-4} C_o + 0.940)} \end{aligned} \tag{14}$$

Equation (14) can be used to derive the amount of CTAB sorbed onto activated carbon at any given initial CTAB concentration and contact time, at the pH 9.9 and within amount of sorbent, 0.10 g.

As can be seen from Table 1, the equilibrium sorption capacities and correlation coefficients for second-order model are much more reasonable when compared with experimental results than those of the first-order system. Since most of the first-order $q_{e,1}$ values deviate significantly from the experimental values it suggests that the sorption of CTAB onto PAC follows the pseudo-second-order model. The regression analysis of second order equation gave a better r_2^2 value. Further, there was very minor deviation between expected and observed $q_{e,2}$ (amount of CTAB adsorbed at equilibrium, mg/g^{-1}) values. It can be said that more than one-step may be involved in sorption process. In addition, for first order model the intercept of the straight line plots of $\log(q_{e,1} - q_t)$ against t should be equal to $\log q_e$. If this is not the case, it suggest that the sorption would not be a first order reaction even if the linearized plots have higher corrleation coefficients than other two mechanisms. From Fig. 2, it is shown that the intercepts of all the straight line plots are different. This suggests that CTAB adsorption does not follow a first order kinetic mechanism.

3.2. *Intraparticle Diffusion Model*

Sorption kinetic data was further processed to determine whether intraparticle diffusion is rate limiting and to find the rate parameter for intraparticle diffusion (k_i). Fraction of CTAB uptake against square root of contact time ($t^{0.5}$) is shown in Fig. 4. For the sorption of CTAB, the correlation coefficients of the intraparticle diffusion model are given in Table 3 for the different initial concentrations and although all are high (>0.975), they are significantly lower than the other is. This suggests that the pseudo-second-order adsorption mechanism is predominant (Ho and McKay, 1998, 2003). As can be seen from Fig. 4, plots of the amount of CTAB per unit weight of PAC against the square root of $t$generates the straight line fits that do not pass through the origin (Fig. 5), indicating that there is a boundary layer resistance. Values of intercepts (Table 3) give an idea about the thickness of boundary layer. That is, the larger an intercept the greater is the boundary layer resistance. Our results show the boundary layer resistance increases with the increasing initial CTAB concentration (see Fig. 5). Intercepts increase from –12.2 to –126.5, while initial concentration changes from 30 to 300 mg/L. This suggests that for CTAB sorption onto PAC the mechanism is predominantly diffusion. Pseudo second order kinetics depicts the involvement of both, the external mass transfer and intraparticle diffusion mechanisms in sorption (Ho and McKay, 1998, 2003). Therefore, the overall rate of the sorption process for CTAB appears to be influenced by the both boundary layer diffusion and intraparticle diffusion.

Double nature plots (non-linear plot) for other workers for physical adsorbents like also observed

Table 3. Pore diffusion coefficients and intraparticle diffusion rate constants, k_i of CTAB onto PAC at different initial CTAB concentrations.

Initial CTAB conc.	Intraparticle diffusion rate constant (mg/gmin$^{-1/2}$)				Intercepts from Eq. (9)	$t_{1/2}$	D (cm^2 s^{-1})	n
(C_0, mg/L)	$k_{i,1}$	$k_{i,2}$	$r^2_{i,1}$	$r^2_{i,2}$	c	(from Eq. (10))	$\times 10^{-6}$	($k_{i,1} = (C_0)^n$)
30	18.69	0.062	0.985	0.650	−12.2	0.41	7.3	0.86
60	36.27	7.25	0.996	0.873	−22.7	0.47	6.4	0.88
90	51.02	3.71	0.992	0.854	−26.3	0.50	6.0	0.87
120	76.04	5.15	0.978	0.602	−54.8	0.54	5.6	0.90
150	94.73	4.79	0.991	0.480	−66.0	0.59	5.1	0.91
180	122.5	1.41	0.997	0.628	−99.5	0.62	4.8	0.93
240	158.9	0.52	0.997	0.600	−132.4	0.70	4.3	0.92
300	178.7	0.87	0.975	0.917	−126.5	0.81	3.7	0.91

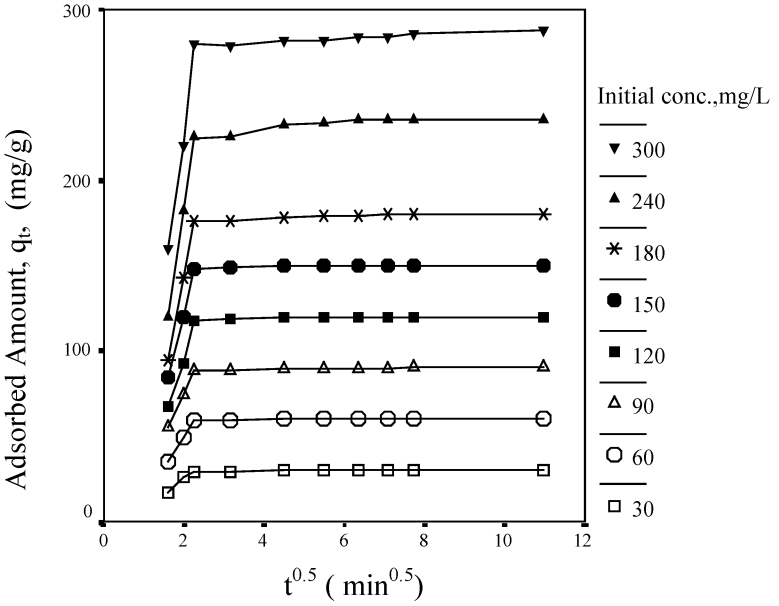

Figure 4. The change of q_t against $t^{0.5}$ at different initial CTAB concentrations for intraparticle diffusion model.

intraparticle model, activated pits (Ho and McKay, 1999), biological adsorbents like chitosan (Juang et al., 2000; Wu et al., 2001) and *Sphagnum* moss peat (Ho et al., 1995). This result confirms that adsorption on PAC has a physical character. Ho and McKay (1999) who suggested that both the diffusion processes (external mass transfer and intraparticle diffusion) have effects on adsorption support the above results. It was provided an explanation for a non-linear plot by a variety of intraparticle diffusion mechanisms (Ho and McKay, 1999, 2000; Erosa et al., 2001).

The multilinearity appearing in Fig. 4 indicates that two or more phenomena occur successively. The first, stage is the external surface adsorption or instantaneous adsorption stage. The second, gradual linear stage is the gradual adsorption stage, where intraparticle diffusion is the controlling factor of the adsorption process. The third, linear stage is the final equilibrium stage where the intraparticle diffusion starts to slow down because of extremely low solute concentration in the solution. Since activated carbon consists of a network of interconnected pores of varying sizes which are classified according to their diameter; micropores <2.0 nm, mesopores 2–50 nm and macropores >050.0 nm, the pores provide a large internal surface area, typically ranging from 800 to 1200 m^2/g, the behavior of

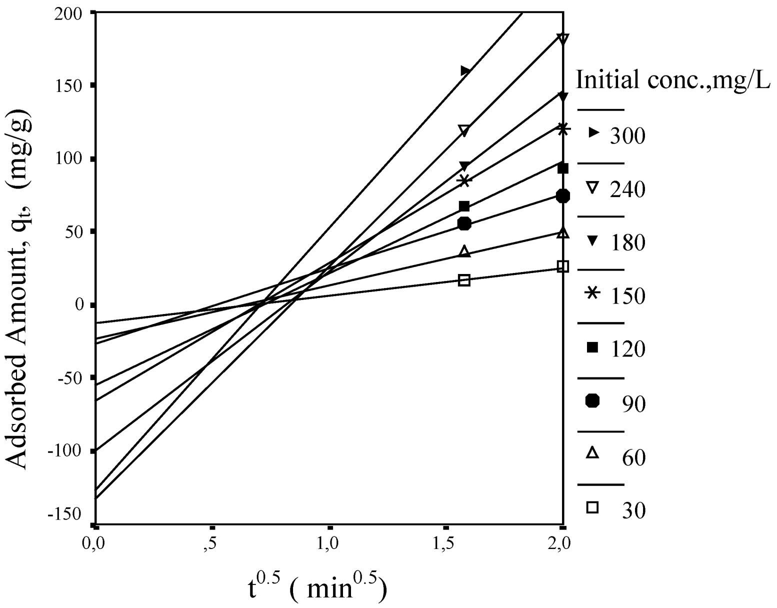

Figure 5. Plot showing closely intercepts, c, in previous figure for intraparticle diffusion model at different initial CTAB concentrations.

multilinearity may also attributed to diffusion in pores with different sizes. As shown in Fig. 4, the instantaneous adsorption in the first stage is not absent in the working range and completed within about 5 min. The second stage due to intraparticle diffusion, being rate-controlled, is immediately attained at the beginning (nearly in 5 min) of the adsorption process. The third section of the figure is due to a drop in diffusion rate. That is, final equilibrium stage is nearly attained. In other words, the CTAB molecules are slowly transported via intraparticle diffusion into the particles and are finally retained in micropores. A good correlation of rate data with the linearized form of the model indicates that diffusion mechanisms control the rates. The intraparticle diffusion constants could be calculated using Eq. (9). In general, the slope of the lines in each stage is called the rate parameter k_i. Table 2 presents intraparticle diffusion (not boundary diffusion due to absent first stage) constants ($k_{i,1}$, $k_{i,2}$). The $k_{i,1}$ and $k_{i,2}$ express intraparticle diffusion rates of the second and third stages in the adsorption (Meshko et al., 2001; Basibuyuk and Forster, 2003; Singh et al., 2001).

From Table 3, it is seen that the order of adsorption rate was the first stage ($k_{i,1}$) $>$ second stage ($k_{i,2}$). It can be said the CTAB was adsorbed by the exterior surface of PAC particle at the beginning, so the adsorption rate was very fast. When the adsorption of the exterior surface reached saturation, the CTAB entered into PAC particle by the pore within the particle and was adsorbed by the interior surface of the particle. When the CTAB diffused in the pore of the particle, the diffusion resistance increased, which caused the diffusion rate to decrease. With decrease of the CTAB concentration in the solution, the diffusion rate became lower and lower and the diffusion processes reached the final equilibrium stage. Therefore, the changes of $k_{i,1}$and $k_{i,2}$ could be attributed to the adsorption stages of the exterior surface, interior surface and equilibrium, respectively. Allen et al. (1997) thought that there were four separate regions depicting the mass transfer, i.e. external mass transfer effect, macropore diffusion, transitional pore diffusion and micropore diffusion. Table 3 shows that all of $k_{i,1}$ and $k_{i,2}$ increased with initial CTAB concentration. The driving force of diffusion was very important for adsorption processes. Generally the driving force changes with the CTAB concentration in bulk solution. The increases of CTAB concentration result in increase of the driving force, which will increase the diffusion rate of the CTAB ions in pore (Annadurai et al., 2000; Sun and Yang, 2003; Li et al., 1999; Mohana et al., 2002).

The data compiled in Table 3 show the initial rate of intraparticle diffusion increase with increase in CTAB concentration. The result of Table 3 can be further explained by the formula $k_i = (C_0)^n$ where, n, a constant (see Table 3), which indicates that initial intraparticle rate parameter (k_i) is directly related to the square root of the initial CTAB concentration, C_0 (2,11). The values of n for all initial CTAB concentrations were >0.86, indicating thereby that intraparticle diffusion is not the sole operative mechanism. These results are supported by those of Ho and McKay (1998, 1999, 2003).

The pore diffusion coefficients were determined from Eq. (10). The rate of adsorption and the magnitude of D (see Table 3) are dependent upon the nature of the adsorption process, for physisorption processes the magnitude of D ranges from 10^{-2}–10^{-5} cm^2/s and for chemisorption systems 10^{-5}–10^{-13} cm^2/s. This may be explained by the stronger bonds holding the molecules tighter to the adsorbent pore walls thus lowering the rate (Walker and Weatherley, 1999). However, D values for CTAB sorption onto PAC varied with change in initial CTAB concentration. Diffusivity should be independent of bulk solute concentration. However, it was reported an increase in solid diffusivity with concentration during the adsorption of nitrobenzene onto activated carbon (Walker and Weatherley, 1999). In contrast, our results indicate that there is a decrease from $7.3 \cdot 10^{-6}$ to $3.7 \cdot 10^{-6}$ cm^2/s in diffusivity with increasing CTAB concentration. A possible explanation for the decrease in diffusivity with increasing initial concentration of CTAB displayed by the CTAB/PAC adsorption system, may be the tendency for CTAB molecules to form micelles at high concentration. The other possibility is that due to the increased size of the sorbing molecules, access to the porous structure of the adsorbent particle may be denied (Allen et al., 1997).

4. Conclusion

The current work focussed on sorption of CTAB from aqueous solutions onto activated carbon for a better understanding of the kinetics. The results present in this paper show the sorption is a physical, with D ranging from 10^{-2}–10^{-5} cm^2/s, which is a characteristic for physisorption processes. That the sorption reach to the equilibrium in nearly 5 min supports the conclusion. Although intraparticle diffusion played a significant role, it was not the main rate determining step throughout the adsorption. Both intraparticle diffusion and boundary layer diffusion seem significant in the rate controlling step. A comparison of the kinetic models on the overall adsorption rate showed that CTAB/PAC system was best described by the pseudo second order rate model and sorption can not been described with first order model. The pseudo-second order sorption kinetics at a constant sorbent dosage with the parameters themselves directly varying with CTAB concenration. Based on the parameters derived, the amount of CTAB sorbed q_t at any given time t, can be predicted for any given concentration from Eq. (14).

Notation

q_t	Adsorbed amount at t time
q_e	Adsorbed amount at equilibrium
t	Time
k_1	Rate constant for first order model
k_i	Rate constant for first order model
$t_{\frac{1}{2}}$	Half- time for adsorption
r_0	Average mean size of adsorbent
D	Pore diffusion coefficient
A_q	Coefficient in Eq. (11)
B_q	Coefficient in Eq. (11)
A_h	Coefficient in Eq. (12)
B_h	Coefficient in Eq. (12)
A_{k2}	Coefficient in Eq. (13)
B_{k2}	Coefficient in Eq. (13)
h	Initial adsorption rate
k_2	Rate constant for second order model
n,	A constant
C_0	Initial concentration

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