Kinetics of Phenol Removal from Aqueous Solution by Adsorption onto Peanut Shell Acid-activated Carbon

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ABSTRACT: A pseudo-second-order rate equation describing the kinetic adsorption of phenol onto peanut shell acid-activated carbon at different initial concentrations, carbon dosages and particle sizes has been developed. The adsorption kinetics were followed on the basis of the amount of phenol adsorbed at various time intervals at 22°C. The rate constant and the equilibrium adsorption capacity were calculated. From these parameters, empirical correlations for predicting the equilibrium adsorption capacity as a function of the C_0/D ratio, and for estimating the rate constant as a function of the relation $D/(C_0d_p)^{0.5}$, were derived.

This allowed a general rate expression for design purposes to be obtained which was valid for $C_0/D \leq 1.5$. The operation line for each case studied was constructed and the equilibrium adsorption capacity obtained. A comparison was undertaken with the experimental adsorption isotherm as previously determined. The effect of the initial phenol concentration, the carbon dose and the particle size on the initial adsorption rate was also analyzed.

INTRODUCTION

The adsorption of organic molecules from water onto activated carbon has gained increasing interest during the past decade. Activated carbons are widely used for separation and purification processes involving aqueous solution systems. To design adsorption equipment, it is necessary to know the adsorption capacity as well as the rate of adsorption.

A series of studies has been conducted in our laboratory to prepare and characterize activated carbons obtained from peanut shell. Recently, Romero *et al*. (2003) and Gonzo (2003) have shown that activated carbon obtained from peanut shell treated with phosphoric acid has a high specific surface area and pore volume, as well as exhibiting a large adsorption capacity towards organic molecules. These authors have also presented the equilibrium adsorption isotherm for a series of organic compounds together with a correlation for estimating them.

In the present work, the kinetics of phenol adsorption from aqueous solution onto activated peanut shell carbon are presented. Studies of sorption kinetics in the removal of phenol from aqueous effluents using different activated carbons have been reported by several researchers. Thus, Peel *et al*. (1981) used the branched-pore-diffusion model for measuring the adsorption rate of phenol onto Filtrasorb F400 carbon. They determined the external mass-transfer coefficient, surface diffusion and kinetic constants for the model. Calleja *et al*. (1993) compared three kinetic models: (i) a simple external resistance model, (ii) a linear model assuming a linear isotherm and

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negligible external mass-transfer resistance and (iii) a pore-diffusion model assuming a non-linear isotherm. The best reproduction of the adsorption decay curves was given by the pore-diffusion model. However, despite its simplicity, the linear model also provided good agreement with the experimental data.

Nevscaia *et al*. (1999) showed that diffusion within the porous structure of non-modified carbons controls the adsorption rate, while the controlling step on oxidized carbon is adsorbate–surface interaction. These workers observed that the adsorption of phenol on oxidized carbon was substantially less than that on the untreated material. Indeed, an important study on the effect of the chemical composition of the carbon surface on the adsorption of phenol and related kinetics was reported by Terzyk (2003), who related the energy of phenol diffusion to the values of the various physicochemical parameters of the carbon studied. He also showed that phenol diffusion is a mixed process involving a surface process and one in the carbon pores. Tseng *et al*. (2003) studied the adsorption kinetics of phenols and dyes on pinewood-based activated carbons using simpler models. Al-Asheh *et al*. (2003), on the other hand, determined the capacity of physically and chemically activated bentonites to adsorb phenol from aqueous solutions.

Although several complex models (the pore-diffusion model, branched-pore-diffusion model, heterogeneous effective diffusivity model) have been applied to describe the transport of molecules inside the adsorbent particles in batch processes, the mathematical complexity of these models makes them inconvenient for practical uses. As was pointed out nearly 40 years ago by Aris (1966) and more recently Levenspiel (2002), what is really needed are simple models that can provide a good description of the system behaviour.

In the present studies, the pseudo-first and -second-order equation models (Wu *et al*. 2001), the intraparticle diffusion model and the Elovich equation (Aharoni and Tompkins 1970) have been tested. General correlations between the fundamental parameters of the models with variables such as the initial adsorbate concentration, the carbon particle size and dosage were developed. These data and the general kinetic expressions established could be useful in further applications for water treatment and process design.

EXPERIMENTAL

Batch kinetic studies were carried out in a glass vessel (volume, 0.6 dm³; i.d., 80 mm; height, 120 mm) fitted with four glass baffles of 25 mm width which were distributed evenly. A known volume (0.3 dm³) of phenol solution was poured into the vessel and agitated with a cylindrical magnetic impeller (30 mm length, 10 mm width) at 500 rpm. Stirring speeds higher than 500 rpm had little effect on the adsorption rate. The initial concentration of the aqueous phenol solution was in the range 0.5–1.5 mmol/dm³. All experiments were carried out at 22°C. The solution concentrations were determined by means of a UV–vis spectrophotometer (Beckman DU 520) at 268 nm. Activated carbon samples of 30–50, 60–80 and 100 Tyler Mesh size were employed at a dosage, D, in the range 0.8–6.0 g/dm³. Before use, the carbon samples were treated overnight in a vacuum oven at 130°C.

After adding the carbon sample to the glass vessel, samples of the solution were taken at pre-set time intervals and their phenol concentrations measured. All samples were re-introduced into the vessel immediately after UV estimation to eliminate errors arising from sampling losses.

The amount of phenol adsorbed, q (mmol/g), at a time t (s) was calculated from the relationship:

$$q = \frac{(C_0 - C_t)}{D} \qquad (1)$$

where C_0 and C_t (mmol/dm^3) are the initial phenol solution concentration and that measured at any time t, respectively.

RESULTS AND DISCUSSION

Activated carbon: physical and adsorptive characterization

The physical characteristics of the activated carbon studied have been reported previously (Romero *et al*. 2003). The corresponding pore volume, surface area and pore-size distribution data are listed in Table 1.

The equilibrium adsorption isotherm data for phenol onto this activated carbon obeyed the Freundlich equation (Romero *et al*. 2003; Gonzo 2003) for equilibrium concentrations up to 7 mmol/dm^3:

$$q_e = 1.235C_e^{0.443} \tag{2}$$

where q_e is the equilibrium adsorption capacity at the equilibrium concentration C_e.

Kinetic adsorption models

To explain the adsorption mechanism, the experimental data were tested using four kinetic models. These are listed below.

Pseudo-first- and -second-order models

As given by Cheung *et al*. (2001), the general equation for pseudo-first- and -second-order kinetics may be written as:

$$\frac{dq}{dt} = k_n(q_e - q)^n \tag{3}$$

where k_n is the rate constant, n the model order and q_e the equilibrium adsorption capacity.

When n = 1, integration of equation (3) with the initial condition that q = 0 at t = 0 leads to the following relationship:

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{4}$$

TABLE 1. Properties of the Activated Carbon Studied

S_g (BET) (m^2/g)	S_g (iodine) (m^2/g)	V_T (P/P^0 = 0.95) (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	L_m (nm)	Maximum of bimodal PSD peaks (nm)
1735	1693	1.12	0.91	0.21	1.3	0.8–1.6

When n = 2, integration of equation (3) with the same initial conditions leads to:

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

Thus, for the pseudo-first- and -second-order models, the phenol uptake as a function of time can be expressed via equations (6) and (7), respectively:
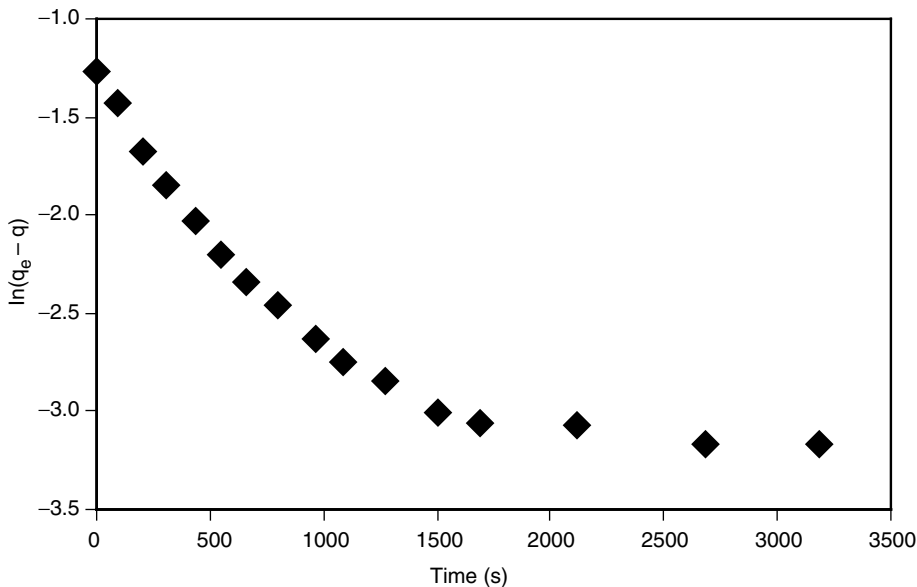
Pseudo-first-order model $\qquad q = q_e\left[1 - \exp(-k_1 t)\right]$ $\qquad\qquad$ (6)

*Pseudo-second-order model* $\qquad q = \dfrac{q_e^2 k_2 t}{1 + q_e k_2 t}$ $\qquad\qquad$ (7)

As can be seen from Figure 1, the pseudo-first-order equation gave a poor fit to the experimental data points. However, Figure 2 demonstrates that the pseudo-second-order equation gave an excellent fit. The correlation coefficients, r^2, for all the experimental runs performed over the whole time range studied were always greater than 0.997. The reproducibility of the measurements was within 5%.

Intraparticle diffusion model

The intraparticle diffusion model is characterized by a linear relationship between the amount adsorbed (q) and the square root of the time (McKay 1983). However, in contrast to the linear plot obtained when the pseudo-second-order model was applied to the experimental data, application of the intraparticle diffusion model led to a plot consisting of at least three straight-line

Figure 1. Test of the pseudo-first-order model for describing the kinetics of phenol adsorption from aqueous solution onto peanut shell activated carbon. Experimental conditions: $C_0 = 0.511$ mmol/l; $D = 1.67$ g/l; $d_p = 0.21$ mm.
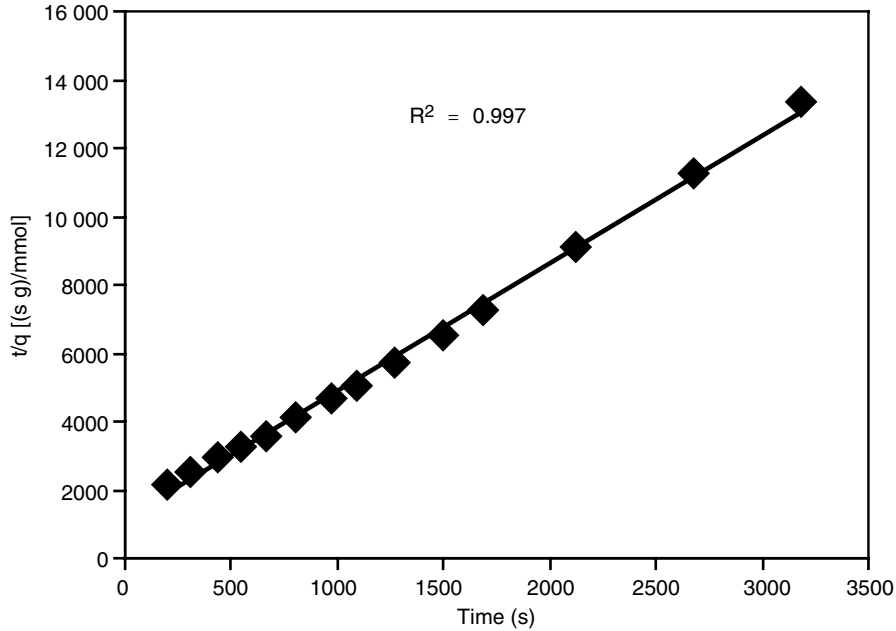
Figure 2. Test of the pseudo-second-order model for describing the kinetics of phenol adsorption from aqueous solution onto peanut shell activated carbon. Experimental conditions: $C_0 = 0.511$ mmol/l; $D = 1.67$ g/l; $d_p = 0.21$ mm.

sections (Figure 3). Each section may be assigned to a different step in the adsorption process. These results confirm that intraparticle diffusion does not provide a fully effective model for this system.

The Elovich adsorption equation

The Elovich equation (Aharoni and Tompkins 1970) was also studied as a means of correlating the experimental data:

$$\frac{dq}{dt} = a \exp(-bt) \tag{8}$$

where a and b are constants during any one experiment. Application of equation (8) is usually tested by converting it to the integrated form, viz.

$$q = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln\left(t + \frac{1}{ab}\right) \tag{9}$$

and assuming $q = 0$, $t = 0$ as the lower limit of integration. For large values of t, i.e. $t \gg 1/ab$, the plot of q versus ln t should be linear.

As can be seen from Figure 4, the data for the adsorption of phenol onto the activated carbon studied gave a plot which was convex to the ln t axis at extended time periods. According to the Elovich equation, any such deviation from linearity should occur at smaller values of t, i.e. the reverse of the situation depicted in the figure. However, a good linear relationship was found over the range $q/q_e \leq 0.6$–0.7.
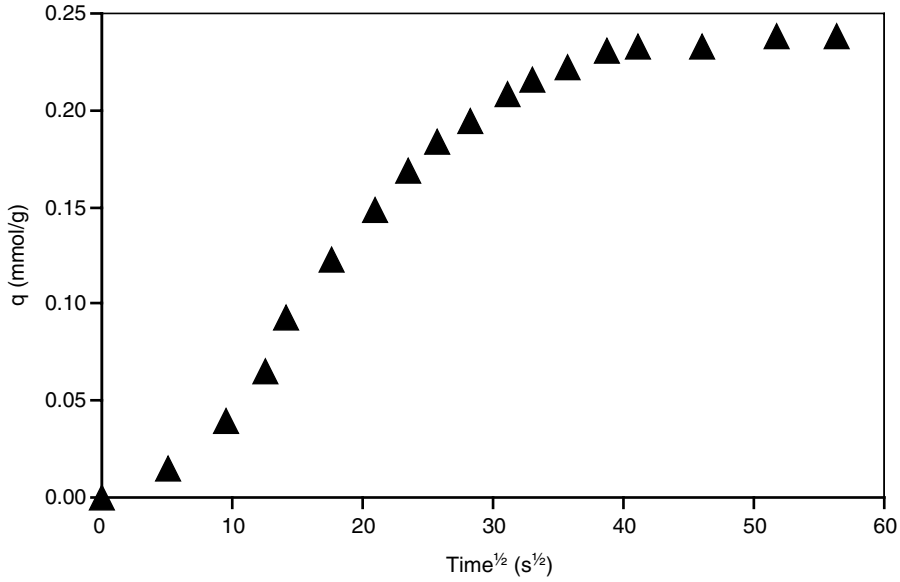
Figure 3. Test of the intraparticle diffusion model for describing the kinetics of phenol adsorption from aqueous solution onto peanut shell activated carbon. Experimental conditions: $C_0 = 0.511$ mmol/l; $D = 1.67$ g/l; $d_p = 0.21$ mm.
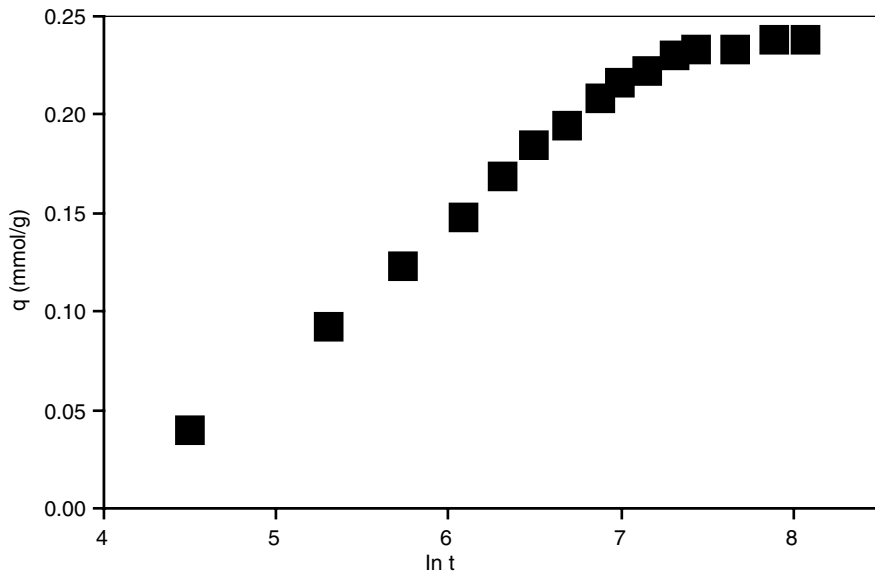
Figure 4. Test of the Elovich equation for describing the kinetics of phenol adsorption from aqueous solution onto peanut shell activated carbon. Experimental conditions: $C_0 = 0.511$ mmol/l; $D = 1.67$ g/l; $d_p = 0.21$ mm.

Applicability of the kinetic models

The applicability of the above models was checked by attempting to obtain a linear fit of the experimental data by the appropriate equations (Figures 1–4). The parameters of the different equation models were determined by minimizing the distance between the experimental data points and the model predictions (σ^2). The normalized standard deviation (Er%) was also calculated. Table 2 lists the results obtained from a typical experiment which indicate that the pseudo-second-order kinetic equation provided the best model for describing the adsorption of phenol onto peanut shell activated carbon.

Figures 5 and 6 illustrate typical curves for the effect of carbon dose, particle size and initial phenol concentration on the adsorption of phenol from aqueous solution onto peanut shell

TABLE 2. Kinetic Parameters and Normalized Standard Deviation (Er%) for Phenol Adsorption onto Acid-activated Peanut Shell Carbon at 22°C[a]

Pseudo-first-order model			Pseudo-second order model			Elovich equation		
k_1 (s^{-1})	q_e (mmol/g)	Er%	k_2 [g/(mmol s)]	q_e (mmol/g)	Er%	1/b (mmol/g)	1/ab (s)	Er%
2.27×10^{-3}	0.2367	8.9	9.56×10^{-3}	0.2800	6.7	6.17×10^{-2}	38.4	14.1

[a]Experimental conditions: $C_0 = 0.51$ mmol/dm^3; D = 1.67 g/l; d_p = 0.21 mm.
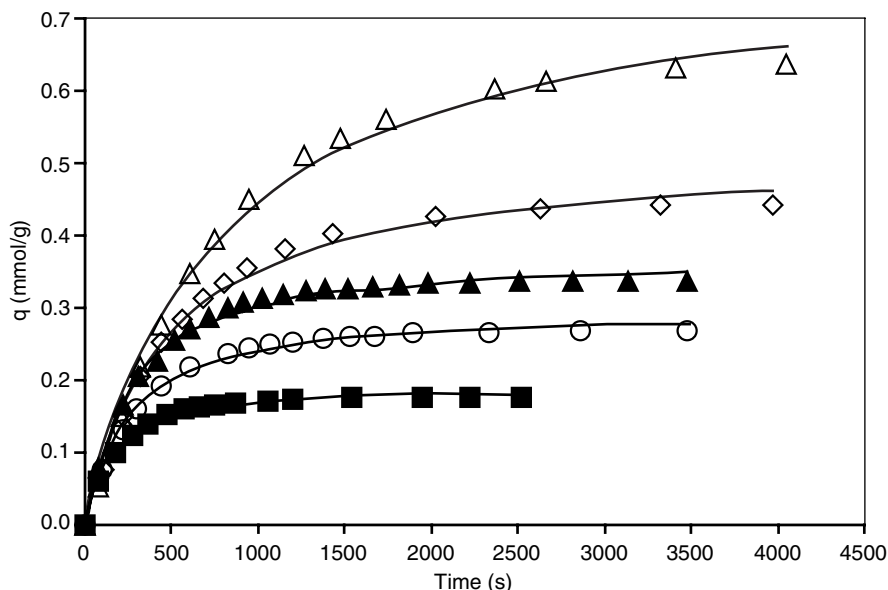
Figure 5. Variation with time of the capacity of peanut shell activated carbon towards the adsorption of phenol from aqueous solution at the following solid/liquid ratios: △, 0.83; ◇, 1.67; ▲, 2.50; ○, 3.33; ■, 5.00. Open symbols relate to a particle size diameter, d_p, of 0.45 mm; filled symbols correspond to a particle size diameter of 0.21 mm. Experimental conditions: $C_0 = 1.03$ mmol/l; agitation speed = 500 rpm.
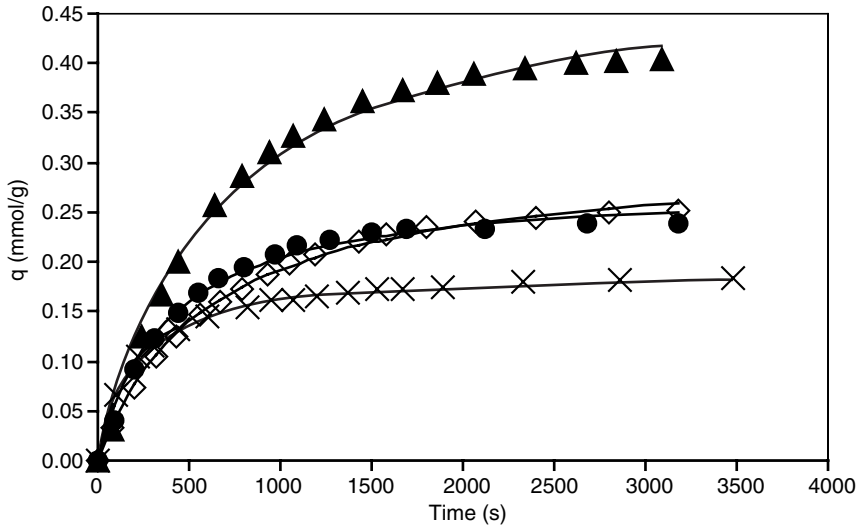
Figure 6. Variation with time of the capacity of peanut shell activated carbon towards the adsorption of phenol from aqueous solution at the following solid/liquid ratios: ▲, 0.83; ◇, 1.67; ●, 1.67; ×, 2.50. Open symbols relate to a particle size diameter, d_p, of 0.45 mm; filled symbols relate to a particle size diameter of 0.21 mm; × symbols relate to a particle size diameter of 0.14 mm. Experimental conditions: $C_0 = 1.03$ mmol/l; agitation speed = 500 rpm.

activated carbon. Again, the theoretical curves derived from the pseudo-second-order model fit the experimental points well over the whole time range studied. These plots show that for all carbon doses, the amount of phenol adsorbed initially increased rapidly with time and then slowed down towards the end of the process. The plots also show that the extent of adsorption at any specific time increased for lower carbon dosages. Deviation of the pseudo-first-order model or the Elovich equation from the experimental data points became more important as the carbon dosage decreased. In contrast, the maximum deviation from the pseudo-second-order model was ca. 7% and decreased as the carbon dose diminished.

With the aim of generalizing the pseudo-second-order kinetic equation, correlations were developed between the equation parameters q_e and k_2 and the independent variables in the system, i.e. the initial phenol concentration (C_0), the carbon dose (D) and the particle diameter (d_p). The correlation equation for q_e may be written as:

$$q_e = -0.027816 + 1.18298 \left(C_0/D \right) - 0.42263 \left(C_0/D \right)^2 \tag{10}$$

This equation only depends on the quantity C_0/D and is independent of the carbon particle size (d_p), as would be expected for a homogeneous adsorbent. Application of the equation to the experimental data obtained in this study is depicted in Figure 7 where the fit observed corresponded to $\sigma^2 = 1.683 \times 10^{-4}$ and Er% = 1%. It was found that the relationship was valid for $C_0/D \leq 1.5$.

Similarly, the correlation equation between k_2 and the initial phenol concentration, carbon dosage and carbon particle size may be expressed by equation (11):
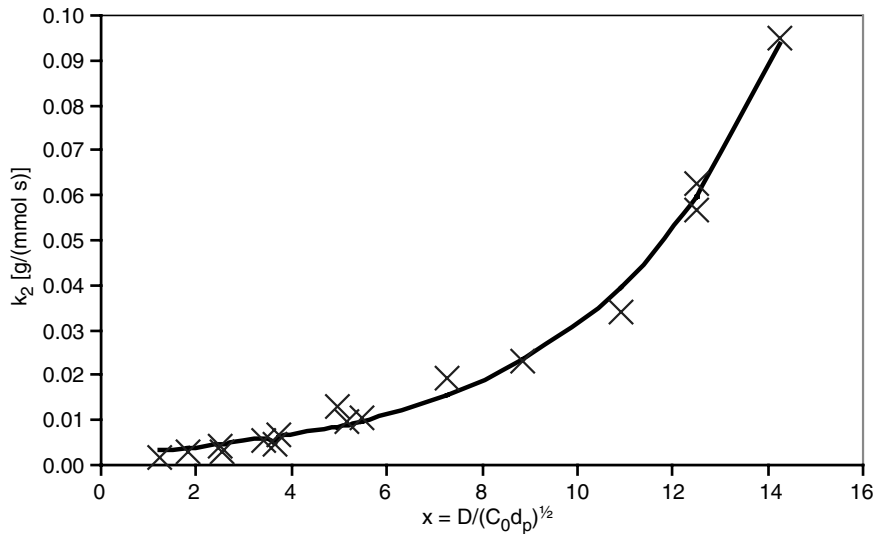
$$k_2 = 2.3616 \times 10^{-3} \exp(0.2584x) \tag{11}$$

where $x = D/(C_0 d_p)^{1/2}$ with d_p being in mm. Application of this correlation equation to the experimental data is depicted in Figure 8 where the fit corresponds to $\sigma^2 = 7.69 \times 10^{-5}$ and Er% = 5.6%.
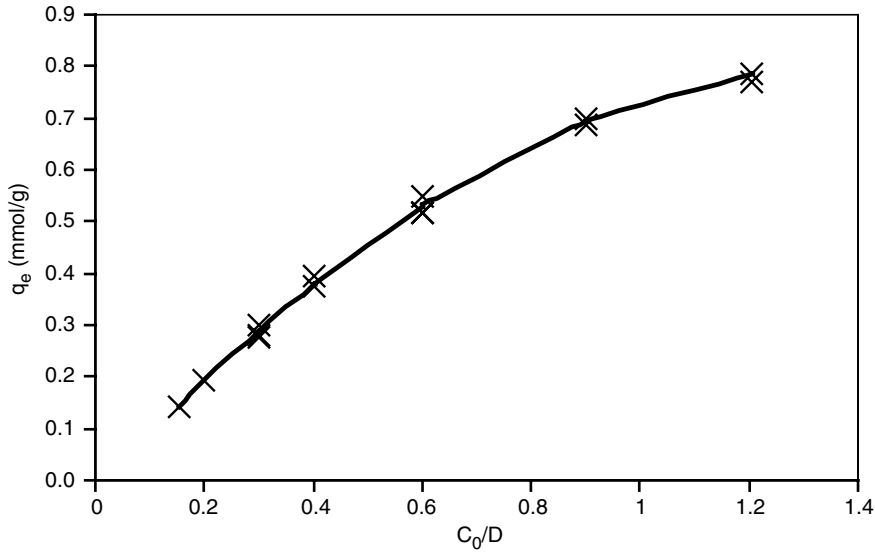
Figure 7. Correlation between the amount adsorbed q_e (mmol/g) and the quantity C_0/D for the adsorption of phenol from aqueous solution onto peanut shell activated carbon.


Figure 8. Correlation between the rate constant k_2 [g/(mmol s)] and the quantity $x = D/(C_0 d_p)^{1/2}$, where d_p is the particle diameter expressed in mm, for the adsorption of phenol from aqueous solution onto peanut shell activated carbon.

Equations (7), (10) and (11) represent a generalized predictive model for phenol adsorption at a given contact time linking the initial phenol concentration, carbon dosage and particle size. Considering the extent of the normalized standard deviation for each case studied and the empirical correlation obtained, it may stated that the pseudo-second-order adsorption equation can be used safely for fitting the kinetic data for the adsorption of phenol onto the acid-activated carbon studied.

Equilibrium capacities from the pseudo-second-order adsorption kinetic equation

The equilibrium capacities q_e predicted by the pseudo-second-order model were compared with the experimental values obtained from the adsorption isotherm. Equation (7) can be used to link q to C_t with the resulting relationship for increasing time being known as the "operation line". Such lines are shown in Figure 9 where the effects of the initial phenol concentration and the carbon dosage at two particle sizes on the adsorption capacity are illustrated. Thus, the line connecting the point C_0, t = 0 on the abscissa to the equilibrium isotherm $q_e = f(C_e)$ has a slope of $-1/D$ (Lazaridis and Asouhidou 2003). Figure 9 also shows the equilibrium adsorption line which is well fitted by the Freundlich equation, i.e. equation (2) (Romero *et al*. 2003). As can be seen, for a given carbon dosage, the final equilibrium concentration and adsorption capacity are the same irrespective of the adsorbent particle size employed. This demonstrates that the activated carbon employed was homogeneous.

Such consistency tests for the experimental data and their treatment are valuable. Thus, the close agreement between the experimental (Freundlich) equilibrium adsorption capacities and
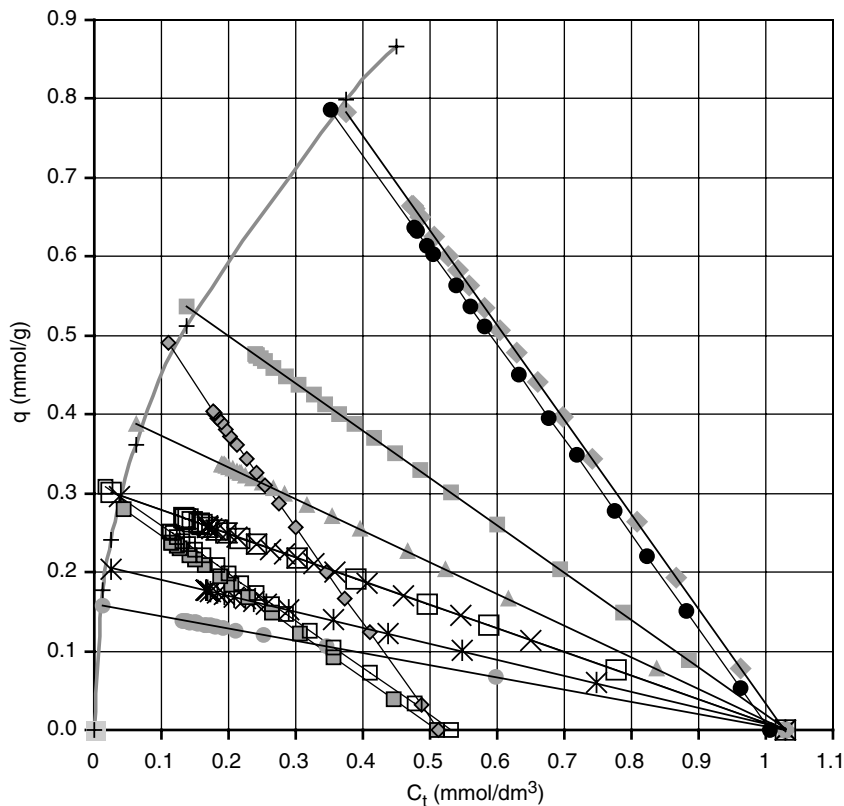
Figure 9. Operating lines and equilibrium adsorption isotherm at various initial phenol concentrations, carbon dosages and particle sizes. Data points relate to the following solid/liquid ratios: ◆, 0.83; ■, 1.67; ▲, 2.50; ×, 3.33; ✳, 5.0; ●, 6.53; +, equilibrium values. Open symbols relate to a particle size diameter, d_p, of 0.45 mm; filled symbols relate to a particle size diameter of 0.21 mm.

those predicted by the pseudo-second-order model shows that the latter is more suitable for describing the adsorption kinetics than any of the other models tested.

External mass-transfer coefficient

It was found that stirring speeds greater than 500 rpm had little effect on the overall adsorption, even when different carbon particle sizes were employed. To shed more light on this observation, the external mass-transfer coefficients k_f (cm/s) were calculated with the assumption that at $t = 0$ the adsorption rate is only controlled by external mass-transfer resistance, i.e. intraparticle diffusion resistance is negligible. Since the phenol concentration on the solid surface is zero at $t = 0$, this can be expressed by the relationship:

$$\lim_{t=0}\frac{dq}{dt} = k_f A C_0 \tag{12}$$

where A (cm^2/g) is the total external surface area of the particles per unit weight of carbon. From equation (7), we can also write that:

$$\lim_{t=0}\frac{dq}{dt} = q_e^2 k_2 = V_I \tag{13}$$

Hence, from equations (12) and (13) it follows that:

$$k_f = \frac{q_e^2 k_2}{A C_0} \tag{14}$$

Table 3 lists the values of the mass-transfer coefficient calculated from the experimental data for several runs employing different initial phenol concentrations, particle sizes and solid/liquid ratios. The results indicate that the whole range of system conditions could be described by a single value of k_f. This is not surprising since k_f would be related to the hydrodynamics of the system

TABLE 3. Values of the External Mass-transfer Coefficient, k_f, Calculated from the Experimental Data Obtained

Run No.	C_0 (mmol/dm^3)	D (g/l)	d_p (mm)	$10^3 k_f$ (cm/s)
1	0.53	2.5	0.14	3.03
2	1.03	1.67	0.14	3.18
3	1.01	3.33	0.14	2.99
4	1.49	3.33	0.14	2.75
5	0.51	5	0.21	4.31
6	1.03	2.5	0.21	2.99
7	1.03	1.67	0.21	3.85
8	1.49	5	0.21	2.98
9	0.53	1.67	0.45	4.76
10	1.03	2.5	0.45	4.31
11	1.03	3.33	0.45	3.48
12	1.48	5	0.45	3.09

which will be constant because of the constant stirring speed and the rather narrow range of carbon particle sizes employed in the experiments. Sherwood *et al.* (1975) have pointed out that, once the particles are suspended in suspensions of solid particles in a liquid, the value of k_f increases slowly with a further increase in the impeller speed. In addition, although the influence of the particle diameter is important over the range of small particle sizes (< 0.01 mm), its relevance almost disappears for particle diameters greater than 0.1 mm.

Effect of the initial phenol concentration, carbon dosage and particle size on the initial adsorption rate

According to equations (10) and (11), values of the initial adsorption rate, V_I [equation (13)], can be calculated as a function of q_e and k_2. In addition, the rate of change of V_I can be determined from the derivative of V_I with respect to each variable. When dV_I/dC_0 is always positive, the initial rate of adsorption increases with increasing initial phenol concentration for any combination of carbon particle size and dose. Similarly, when dV_I/dd_p is always negative, the initial adsorption rate will increase as the particle size decreases. However, it is not possible to define the effects of a small increase in carbon dosage on V_I since this depends on the particular combination of initial phenol concentration and carbon particle size employed. Nevertheless, for given values of C_0 and d_p, V_I has high values at low values of D (0.83–1.67), reaches a minimum at D values between 2.5 and 3.33 and increases when $D \geq 3.33$. This implies that $dV_I/dD < 0$ for low values of D, $dV_I/dD = 0$ at intermediate values of D and $dV_I/dD > 0$ for D > 3.33.

CONCLUSIONS

The pseudo-second-order rate equation has been successfully used to describe the kinetics of phenol adsorption onto acid-activated peanut shell carbon. Use of this model enabled the equilibrium capacity of the adsorbent to be predicted accurately. The normalized standard deviation of the pseudo-second-order model was lower than that for application of the Elovich equation and the pseudo-first-order model to the experimental data. In addition, the predictions of the Elovich equation deviated from the experimental points at higher time values in contrast to the situation displayed by the pseudo-second-order rate equation [equation (9)]. Furthermore, the pseudo-first-order model deviated considerably from linear behaviour, [equation (4)], with increasing time. The pseudo-second-order kinetic model is also more suitable than the other models tested in terms of its better prediction of the equilibrium sorption capacity.

In order to generalize the kinetic expression, correlations were developed for estimating q_e and k_2 as functions of C_0, D and d_p. The generalized predictive model obtained was used to derive the adsorption phenol capacity of the adsorbent for a given initial phenol concentration, carbon dosage and particle size at any particular contact time. The initial sorption rate increases as the initial phenol concentration increases and the particle size decreases. The limited effect of carbon dosage on the adsorption process depends on the particular combination of initial phenol concentration and carbon particle size employed.

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