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ABSTRACT: In this work, the film–pore diffusion model was applied to the adsorption of phenol onto peanut shell activated carbon in a batch stirred vessel. This two-resistance model was applied to predict the phenol concentration decay curves for different initial phenol concentrations, carbon particle sizes and dosages. The predicted concentration decay curves were compared with the experimental findings. The optimum best-fit values of the external mass-transfer coefficient and effective diffusion coefficients were found by minimizing the difference between the experimental and model-predicted phenol solution concentration. It was found that, under the experimental conditions employed in this study, the influence of the external mass-transfer resistance was low. A single value of the mass transport coefficient, $k_f$, of $(4.8 \pm 1.3) \times 10^{-3}$ (cm/s) described the whole range of system conditions. The difference between the corresponding values of the effective diffusivity, $D_{eff}$, was not statistically significant. Consequently, a constant value of the effective pore diffusivity of $(4.1 \pm 0.4) \times 10^{-6}$ (cm$^2$/s) was sufficient to provide an accurate correlation of the decay concentration curve.

1. INTRODUCTION

It is widely recognized that adsorption is one of the more important processes for wastewater treatment. Recently, we published a study of the kinetics of phenol removal from aqueous solution onto peanut shell acid activated carbon (Gonzo and Gonzo 2005) where several simple models were tested. We explained the adsorption mechanism by means of a pseudo-second-order rate equation which gave an excellent fit to the experimental values. It was also shown that the equilibrium capacities obtained from the pseudo-second-order model agreed very well with those found with the experimental Freundlich isotherm (Gonzo and Gonzo 2005). In addition, it was demonstrated that neither the pseudo-first-order rate equation (Tseng et al. 2003), the intraparticle diffusion model nor the Elovich adsorption equation (Aharoni and Tompkins 1970) were capable of describing the rate and extent of phenol adsorption onto an activated carbon particle. Many two-resistance diffusion models exist which describe adsorption processes with varying accuracy (Inglezakis and Pouloupolos 2006; Al-Duri 1996; Choy et al. 2004). However, the film–pore diffusion model (Spahn and Schlunder 1975) has been successfully employed to describe the adsorption of different organic compounds onto several adsorbents (McKay and Bino 1985; Chen et al. 2001a; Hui et al. 2002) as well as the adsorption of metal ions onto bone char (Chen et al. 2001b; Quek and Al-Duri 2007).

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The aim of the present work was to apply the film–pore diffusion model (film mass-transfer resistance and pore diffusion) to predict the concentration versus time decay curves in batch adsorbers.

2. THEORY

The film–pore diffusion model, based on the shrinking core mass-transfer model (Levenspiel 1962), was proposed by Spahn and Schlunder (1975) and applied successfully to several systems by McKay’s group (Al-Duri 1996; Choy et al. 2001a,b, 2004; McKay and Bino 1985; Hui et al. 2002). According to this model, the adsorption rate is controlled by the external and internal mass-transfer resistances. Thus, after the adsorbate arrives at the external surface of the particle, adsorption commences by forming a reaction zone which moves inwards with a defined velocity. During such adsorption, an unreacted core exists which shrinks with time. The fundamental assumptions of the model are:

(a) The corresponding homogeneous model for the porous material is applicable and the mass transfer within the porous carbon particle follows Fick’s law, being given by an effective molecular diffusion.

(b) Equilibrium occurs between the pore solution and carbon surface.

(c) The adsorption is irreversible.

(d) The concentration at the external surface of the carbon particle ($C_R$) remains in equilibrium ($q^0$) as described by the equilibrium adsorption isotherm during the entire adsorption period (Spahn and Schlunder 1975).

(e) Phenol adsorption acquires a quasi-steady state in the carbon particle.

These assumptions imply that the rate of solute adsorption is rapid compared to the motion of the shrinking core front in the solid.

The phenol concentration profile in an activated carbon particle based on this model is depicted schematically in Figure 1. Due to the external mass-transfer resistance in the fluid film surrounding the particle, the phenol solution concentration drops from the value in the bulk fluid ($C$) to a value $C_R$ on the external particle surface. The phenol molecules in the pore solution are transported by molecular diffusion from the external particle surface to the interior. As a consequence, the phenol concentration in the pore solution decreases from $C_R$ to zero on the unreacted core front at $r = r_c$.

The average amount of phenol adsorbed $q$ (mmol/s) at time $t$ (s) is calculated as:

$$ q = \frac{(C^0 - C)}{D} \tag{1} $$

where $C^0$ and $C$ (mmol/dm$^3$) are the phenol solution concentrations at the start of the process and at any time $t$, respectively, while $D$ (g/dm$^3$) is the dosage of activated carbon in the system.

The experimental equilibrium adsorption isotherm data for phenol onto this activated carbon obey the Freundlich equation (Gonzo and Gonzo 2005):

$$ q_e = K_F C_e^n \tag{2} $$
The mass transfer in the external layer is given by:

$$\frac{dq}{dt} = A k_f (C - C_R)$$  \hspace{1cm} (3)

where $k_f$ is the mass-transfer coefficient and $A$ is the total external surface area per unit mass of particles. The coefficient $k_f$ can be determined experimentally by considering that, at $t = 0$, only external mass-transfer resistance controls the adsorption rate ($C_R = 0$). Then:

$$\lim_{t \to 0} \frac{dq}{dt} = A k_f C^0$$  \hspace{1cm} (4)

According to assumption (a) above, diffusion in the spherical porous carbon particle may be expressed as:

$$\frac{dq}{dt} = \frac{AD_{eff} C_R r_f}{R(R - r_f)}$$  \hspace{1cm} (5)

with

$$r_f = R \quad \text{at} \quad t = 0$$

In equation (5), $D_{eff}$ is the effective diffusion coefficient of phenol in the carbon particle.

From assumption (d) above, the average amount of phenol adsorbed at time $t$ (s) is also given by:

$$q = q_e \left[ 1 - \left( \frac{r_f}{R} \right)^3 \right]$$  \hspace{1cm} (6)
where

\[ q_e^b = K_F C_R^b \]  \hspace{1cm} (7)

The velocity of the shrinking core front in the solid is obtained from the mass balance on a carbon particle of density \( \rho_c \):

\[ \frac{dq}{dt} = - \frac{Aq^b \rho_c r_f^2}{R^2} \frac{dr_f}{dt} \] \hspace{1cm} (8)

Equations (1)–(8) define the film–pore diffusion model.

3. EXPERIMENTAL

As in our previous work (Gonzo and Gonzo 2005), kinetic studies were carried out in a glass vessel of 0.6 dm\(^3\) volume, fitted with four baffles and agitated with a cylindrical magnetic impeller at 500 rpm. The initial concentration of the aqueous phenol solution was in the range 0.5–1.5 mmol/dm\(^3\). Activated carbon samples of 30–50 and 60–80 Tyler mesh size were employed at a dosage \( D \), in the range 0.8–6.0 g/dm\(^3\). The solution concentrations were determined by means of a UV–vis spectrophotometer (Beckman DU520) at 268 nm. The physical characteristics of the activated carbon used were: BET surface area = 1735 m\(^2\)/g, pore volume = 1.12 cm\(^3\)/g, mean pore size = 1.3 nm, porosity \( \varepsilon = 0.73 \) and particle density \( \rho_c = 0.65 \) g/cm\(^3\) (Romero et al. 2003).

The kinetics of the overall process were very well described by a pseudo-second-order rate expression (Lagergren kinetics) (Gonzo and Gonzo 2005; Ho 2004):

\[ \frac{dq}{dt} = k_2 (q_e - q)^2 \] \hspace{1cm} (9)

\[ q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \] \hspace{1cm} (10)

The equilibrium adsorption isotherm data for phenol onto this activated carbon obeyed the Freundlich equation (2) with \( K_F = 1.235 \) and \( n = 0.443 \) (Gonzo and Gonzo 2005).

3.1. Application of the film–pore model

By taking advantage of the adsorption rate equations (9) and (10), and considering the equations that define the film–pore diffusion model, it is possible to write the following set of differential equations:

\[ \frac{dC}{dt} = - \frac{DAD_{eff} C_R r_f}{R (R - r_f)} \] \hspace{1cm} (11)

\[ \frac{dr_f}{dt} = - \frac{D_{eff} R C_R^{0.557}}{K_I \rho_c r_f (R - r_f)} \] \hspace{1cm} (12)

These differential equations must be solved with the initial conditions:

\[ C = C^0 \text{ and } r_f = R \text{ at } t = 0 \] \hspace{1cm} (13)
The external surface particle concentration value ($C_R$) may be obtained by combining equations (3) and (9):

$$C_R = C - \frac{k_f(q_e - q)^2}{A_k}$$

(14)

To obtain the concentration decay versus time curve for each batch experiment, the optimum best-fit values of $k_f$ and $D_{eff}$ were found by minimizing the distance between the experimental data point and the model prediction ($\sigma^2$). The normalized standard deviation (Er%) was also calculated.

The Polymath 5.1 program (Polymath 5.1 software 2004) was used to solve the differential equation system (11)–(12) and to obtain the values of the optimum parameters. However, at $t = 0$ ($q = 0; r_f = R; C_R = 0$), the differential equation system is undefined. To overcome this situation, a first step at $t = 0$ is calculated assuming $\Delta r = (R - r_f) = 1 \times 10^{-5}$ cm (Choy et al. 2004); consequently, the values of $\Delta t$ range from 1.7 s to 2.8 s for the different cases studied. The initial guess of $k_f$ was the value obtained from equation (4) with experimental values at $t \to 0$. The effective diffusivity in the model is a function of the molecular diffusivity of phenol in the aqueous solution, the porosity of the carbon particle and the tortuosity ($\tau$) according to:

$$D_{eff} = \frac{D_M \tau}{\tau}$$

(15)

where the molecular diffusivity, $D_M$, of phenol in water was estimated using the Wilke–Chang and Tyn–Calus (Reid et al. 1987) expressions:

$$D_M = \frac{(7.1 \times 10^{-8})(\phi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \quad (\text{cm}^2/\text{s})$$

(16)

$$D_M = 8.93 \times 10^{-8} \left(\frac{V_A}{V_B}^{18} \left(\frac{P_B}{P_A}^{0.6}\right) \frac{T}{\mu_B} \right) \quad (\text{cm}^2/\text{s})$$

(17)

Here, $\phi$ is the solvent association factor, $\mu_B$ is the solvent viscosity (cP), $V_A$, $V_B$ are the molar volume of the solute and solvent, respectively, and $P_A$, $P_B$ are the solute and solvent parachor, respectively. The values of these parameters were found via the Component Plus (ProSim) program (Component Plus 2005). The molecular diffusivity of phenol in water at 295 K was found to be $8.85 \times 10^{-6}$ cm$^2$/s. The initial guess of the effective diffusivity was estimated considering a tortuosity factor of $\sqrt{2}$ (because of the high specific surface area and porosity).

4. RESULTS AND DISCUSSION

The external mass-transfer coefficient ($k_f$) and the effective diffusion coefficient ($D_{eff}$) have been determined for the adsorption of phenol onto peanut shell activated carbon using the film–pore diffusion model. The values of $k_f$, $D_{eff}$, $\sigma^2$ and Er% obtained for the different runs are listed in Table 1.

Figures 2 and 3 show the concentration decay curves obtained experimentally for different solid/liquid ratios (D) and carbon particle sizes, together with the corresponding curves calculated
TABLE 1. Effective Diffusivity and External Mass Transport Coefficient Predicted by the Model

<table>
<thead>
<tr>
<th>Run</th>
<th>C (mM)</th>
<th>D (g/dm³)</th>
<th>Mesh size</th>
<th>$k_i \times 10^3$ (cm/s)</th>
<th>$D_{\text{eff}} \times 10^6$ (cm²/s)</th>
<th>Er%</th>
<th>$\sigma^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.99</td>
<td>1.666</td>
<td>30–50</td>
<td>6.0</td>
<td>4.0</td>
<td>4.4</td>
<td>$6.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>A2</td>
<td>1.00</td>
<td>0.833</td>
<td>30–50</td>
<td>5.1</td>
<td>4.0</td>
<td>2.2</td>
<td>$2.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>A3</td>
<td>1.03</td>
<td>2.500</td>
<td>30–50</td>
<td>5.2</td>
<td>4.0</td>
<td>4.3</td>
<td>$5.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>A4</td>
<td>1.04</td>
<td>3.333</td>
<td>30–50</td>
<td>5.0</td>
<td>4.0</td>
<td>2.9</td>
<td>$1.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>A5</td>
<td>0.53</td>
<td>1.666</td>
<td>30–50</td>
<td>5.0</td>
<td>4.0</td>
<td>2.1</td>
<td>$3.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>B1</td>
<td>0.51</td>
<td>0.833</td>
<td>60–80</td>
<td>5.0</td>
<td>4.8</td>
<td>2.9</td>
<td>$8.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>B2</td>
<td>0.51</td>
<td>1.666</td>
<td>60–80</td>
<td>3.3</td>
<td>4.0</td>
<td>6.7</td>
<td>$3.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>B3</td>
<td>1.03</td>
<td>0.833</td>
<td>60–80</td>
<td>3.3</td>
<td>3.0</td>
<td>2.6</td>
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</tr>
<tr>
<td>B4</td>
<td>1.03</td>
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<td>60–80</td>
<td>5.5</td>
<td>5.0</td>
<td>5.3</td>
<td>$4.1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Figure 2. Sorption of phenol onto activated carbon particles of 30–50 mesh size. Data points correspond to different solid/liquid ratios (D) as listed below the figure. The thin lines depicted in the figure correspond to the application of equations (1) and (10) to the experimental data while the bold line shows the application of the film–pore model.

via the film–pore model. As can be seen from the figures, the agreement between the estimated and experimental concentration data was reasonably good, with a maximum standard deviation $Er\% \approx 6.7\%$ (in case B2, Table 1). This error is almost the same than that obtained using the pseudo-second-order kinetic expression (Gonzo and Gonzo 2005). However, the film–pore diffusion model, although more complex mathematically, is more general and only two parameters ($D_{\text{eff}}$, $k_i$) are needed.
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Figure 3. Sorption of phenol onto activated carbon particles of 60–80 mesh size. Data points correspond to different solid/liquid ratios (D) as listed below the figure. The thin lines depicted in the figure correspond to the application of equations (1) and (10) to the experimental data while the bold line shows the application of the film–pore model.

The variation of the concentration at the external particle surface \( C_R \) as given by application of the model is of interest. Figure 4 shows the profile of \( C_R \) as function of time for three different cases. As can be seen, the profile of \( C_R \) commenced at \( C_R = 0 \) (at \( t = 0 \)), attained a maximum value and then decayed exponentially as expected.

The mean value of the tortuosity factor can be calculated by taking equation (15) into account, resulting in the value \( \tau = 1.6 \). This value of the tortuosity factor is close to \( \sqrt{2} \), i.e. the value of \( \tau \) found for porous materials with a high specific surface area and porosity \( (S_g = 1735 \text{ m}^2/\text{g}; \varepsilon = 0.73) \) (Satterfield 1980; Shen and Chen 2007).

The film–pore diffusion model deviates from the experimental data at high solution concentrations and/or when the dosage (mass/volume ratio) is high and at high contact time. The model over-predicts the adsorption capacity at long contact time because the mathematical expression of the Freundlich isotherm renders it unsuitable for the assumption of an irreversible isotherm which reaches a monolayer saturation capacity [assumption (d)].

Small changes in \( D_{\text{eff}} \) have an appreciable effect on the slope of the concentration decay curves, whereas the value of \( k_f \) had little effect under our experimental conditions. The low sensitivity of \( k_f \) probably arises because the mean values of the Biot number, \( \text{Bi} (= Rk_f/D_{\text{eff}}) \), are 30 and 11, respectively, for the two particle sizes used, viz. 30–50 and 60–80 mesh. Since the Biot number measures the ratio of the internal to the external mass-transfer resistances within the carbon particle, values of \( \text{Bi} > 10 \) are indicative of a relatively low film resistance. The values of \( k_f \) obtained were slightly higher than that obtained from the experimental data at \( t \to 0 \) [equation (4)] (Gonzo and Gonzo 2005), but agreed well with values reported for an adsorption system with a similar Biot number (Quek and Al-Duri 2007).
5. CONCLUSIONS

The film–pore diffusion model has been used successfully to predict the concentration decay curves for the batch sorption of phenol onto a peanut shell activated carbon. The model is very sensitive to variations of $D_{\text{eff}}$, while the magnitude of $k_f$ has little effect. Deviations between the predicted and experimental values of the concentration were observed when high initial phenol concentrations and high adsorbent dosage were used. The deviation found at long contact times was a consequence of the Freundlich adsorption isotherm which is incapable of predicting a saturation capacity (monolayer plateau). The results showed that a single value of the mass-transport coefficient $k_f$ of $(4.8 \pm 1.3) \times 10^{-3}$ (cm/s) described the whole range of system conditions employed in the present work, as was pointed out previously by the authors (Gonzo and Gonzo 2005). The difference between the corresponding values of the effective diffusivity $D_{\text{eff}}$ was not statistically significant. Hence, a constant value of the phenol effective pore diffusivity of $(4.1 \pm 0.4) \times 10^{-6}$ (cm$^2$/s) was sufficient to provide an accurate correlation of the decay concentration curve.

REFERENCES


