THE KINETICS OF ADSORPTION OF PENTACHLOROPHENOL ONTO ACTIVATED CARBON FIBERS FROM AQUEOUS SOLUTION

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Introduction

In the last years, several studies have been carried out about the adsorption of pentachlorophenol (PCP) present in wastewaters onto activated carbon. It has been shown that PCP can be adsorbed on activated carbon but the mass of PCP adsorbed depends significantly upon the solution pH. Various commercial granular and powdered activated carbons, and some manufactured at laboratory scale have been tested thoroughly [1,2].

Recently a new form of activated carbon has been marketed that is prepared by the carbonization and activation of fabrics made from several polymeric materials, such as Nylon, Rayon, cellulose, phenolic resin, poliacrilonitrilo (PAN) and tar pitch [3]. This novel form is known as activated carbon fiber (ACF) and is manufactured in two presentations like cloth and felt. The characteristics of the ACF depend on polymeric fabric used to manufacture the ACF.

The ACF offers several advantages in comparison with GAC and PAC. The porous structure of ACF is mainly comprised of micropores while the GAC and PAC have very complex porous structure formed by micropores, mesopores and macropores. The fiber diameters of the ACF (0.006 to 0.017 mm) are on the average 100 times smaller than the particle diameters of the GAC (1 to 3 mm) and lightly smaller than the particle diameters of the PAC (0.015 to 0.025 mm). Therefore, the adsorption rate in the FCA is much faster than in the GAC and slightly quicker than in the PAC.

Very few studies have been reported on the adsorption of phenolic compounds from aqueous solution onto ACF [4,5]. In general the adsorption capacity of ACF is slightly greater than that of the GAC and PAC. The adsorption rate of PCP in GAC has been investigated but no study has been reported about the adsorption rate of PCP in ACF.

The aim of this work is to study the rate of adsorption of PCP on ACF as well as to assess the effect of intraparticular diffusion on the overall rate of adsorption.

Diffusional Model

It is very well documented in the literature [6] that the overall rate of adsorption can be described by a mechanism of three consecutive steps: i) external mass transport, ii) intraparticle diffusion and iii) adsorption at an interior site. Moreover, intraparticle diffusion in liquid-porous solid systems may be governed by pore volume diffusion or surface diffusion or a combination of both.

A diffusional model was developed to interpret the rate of adsorption of PCP from a finite bath of an aqueous solution on ACF. The model was derived assuming that the fibers are cylindrical with average diameters of 13μm and that intraparticle diffusion is only due to pore volume diffusion. The model equations are:

$$V \frac{dC_A}{dt} = -mS\, k_L \left(C_A - C_{A,R} \right) \tag{1}$$

$$t = 0 \quad , \quad C_A = C_{Ao} \tag{2}$$

$$\varepsilon_p \frac{\partial C_{A,r}}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left[r\left(D_{e,p} \frac{\partial C_{A,r}}{\partial r} \right) \right] \tag{3}$$

$$C_{A,r} = 0 \text{ a } t = 0, 0 \leq r \leq R \tag{4}$$

$$\frac{\partial C_{A,r}}{\partial r}\Big|_{r=0} = 0 \tag{5}$$

$$D_{e,p} \frac{\partial C_{A,r}}{\partial r}\Big|_{r=R} = k_L \left(C_A - C_{A,R} \right) \tag{6}$$

It was also assumed that adsorption occurs instantaneously, thus local equilibrium exists between the adsorbate in the pore liquid and that on the pore surface. Hence, the adsorption isotherm provides the mathematical relationship between $C_{A,r}$ and q. This relation can be represented as follows

$$q = f(C_{A,r}) \tag{7}$$

The partial and ordinary differential equations of this model were solved numerically using the PDESOL software.

Experimental

The activated carbon fiber (ACF) used in this work is manufactured from PAN by the company KoTHmex in the form of Felt (AM1132). The ACF was washed repeatedly with distilled water to remove dust and then dried in a oven set at 383 K during 24 hours.

The concentration of PCP in aqueous solution was determined by UV spectroscopy using a spectrophotometer, Shimadzu, model UV-160. The PCP concentration of a sample was estimated using a calibration curve (absorbance vs. concentration) prepared using five to six standard concentration solutions of PCP.

Experimental adsorption isotherm data were obtained as follows. A predetermined mass of ACF was contacted with a fixed volume of a PCP solution of known initial concentration. The solution remained in contact with the ACF until equilibrium was reached, which took place in 3 to 5 days. The solution pH was adjusted and kept constant by adding 0.01, 0.05 and 0.1 N HNO_3 or NaOH solutions as required. The solution was sampled at certain time intervals, and the concentration of PCP was determined for each sample. Equilibrium was reached when the concentrations of two consecutive samples did not change and the mass of PCP adsorbed at equilibrium was calculated by performing a mass balance.

A flow-through batch adsorber was used to carry out the rate of diffusion experiments. The adsorber consisted of a small column to placed the ACF, a storage vessel and a peristaltic pump. The storage vessel was partially immersed into a constant temperature water bath and set atop a magnetic stirrer to mix the solution. The PCP solution was added to the storage vessel and circulated through the column by means of the peristaltic pump.

A certain mass of ACF was packed in the column and 475 mL of a buffer solution were poured into the storage vessel. Then the pump was turned on to circulate the buffer solution through the column packed with the ACF. The solution pH was kept constant at pH = 12 by adding 0.1 N HCl or NaOH solutions as required. Once the solution pH remained unchanged 25 mL of a solution of known concentration of PCP was added rapidly to the storage vessel and the timer was turned on immediately. The storage vessel solution was sampled periodically and the volume of the solution was kept constant by adding to the storage vessel an equal volume of a make-up solution right after the sample was taken. The concentration of the make-up solution was between the initial and equilibrium concentrations of PCP in the solution. The samples were analyzed to determine the concentration of PCP.

The experimental concentration decay data, the concentration of PCP vs. time, was expressed in dimensionless form as follows:

$$\phi = \frac{C_A}{C_{A0}} \tag{8}$$

The dimensionless concentration, ϕ, was plotted against the time to obtain the dimensionless concentration decay curve.

Results and Discussion

The experimental data for the adsorption of PCP on the ACF was fitted to the adsorption isotherm model of Prausnitz-Radke, this model is represented by the following equation:

$$q = \frac{aC}{1 + bC^\beta} \tag{9}$$

The values of the isotherm constants were evaluated using a least-squares method based on an optimization algorithm. The experimental data and the Prausnitz-Radke isotherm are graphed in Figure 1.
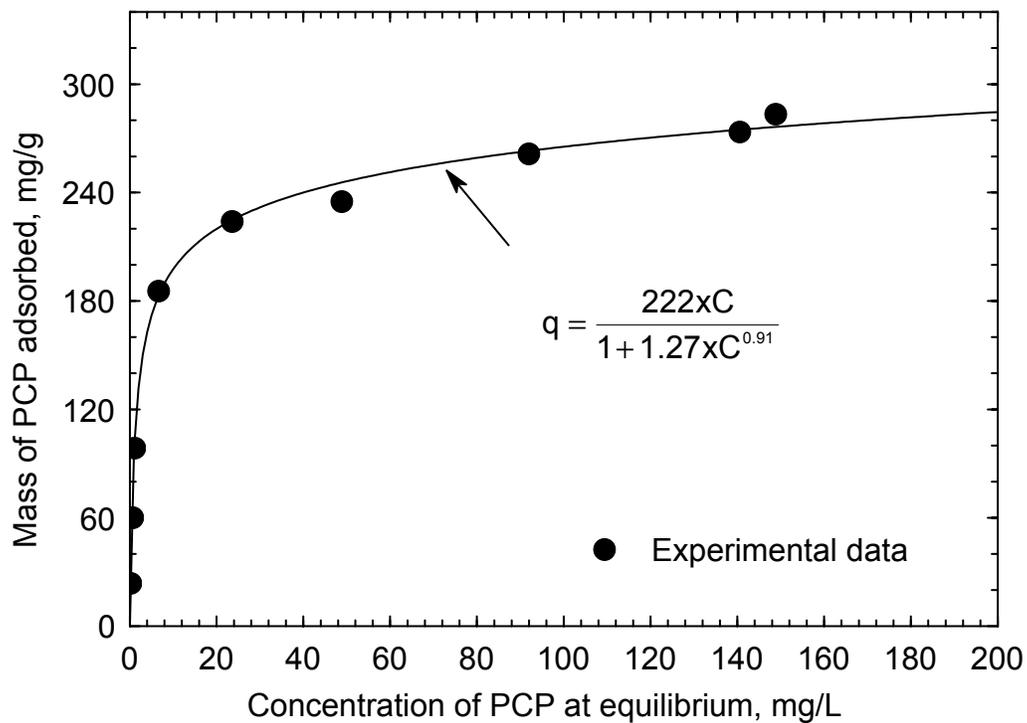

$$q = \frac{222 \times C}{1 + 1.27 \times C^{0.91}}$$

Figure 1. Adsorption isotherm of PCP on ACF

The effective pore volume diffusivity, $D_{e,p}$, and the mass transfer coefficient, k_L, are the only unknown parameters of the diffusional model. The mass transfer coefficient, k_L, was estimated from the initial slope of the concentration decay curve [7]. Then the effective pore volume diffusivity, $D_{e,p}$, was evaluated by matching the experimental concentration decay data to the predicted concentration decay from a numerical solution of the diffusional model. The best value of $D_{e,p}$ is the one that fits the experimental data best using the following objective function:

$$\Sigma(\phi_{exp} - \phi_{pred})^2 \qquad (10)$$

The experimental PCP concentration decay data and the PCP concentration decay predicted with the best value of $D_{e,p}$ are plotted in Figure 2 for one experiment. As it is shown in Figure 2, the diffusional model predicted reasonably well the experimental concentration decay data.
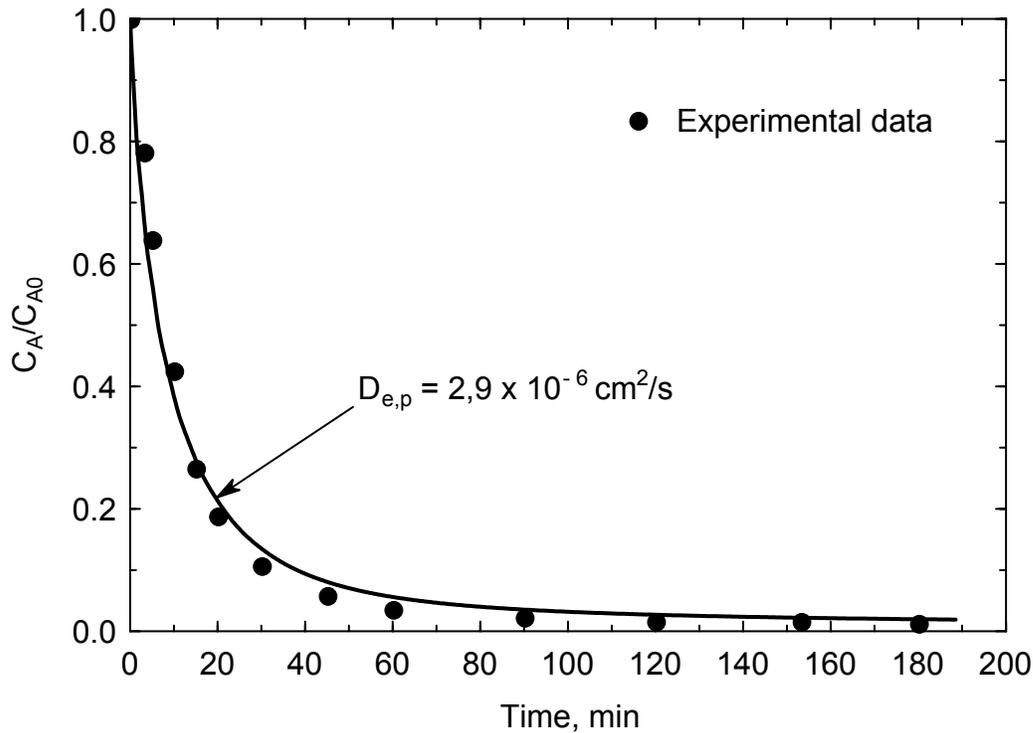

Figure 2. Concentration decay curve for PCP adsorption on ACF.
The lines represent the diffusional model predictions.

The effective pore volume diffusivity, void fraction of the ACF and molecular diffusivity of PCP were used to find the value of the tortuosity factor, τ_p, by

$$\tau_p = \frac{\varepsilon_p D_{AB}}{D_{e,p}} \qquad (4)$$

The void fraction of the ACF was reported to be $\varepsilon_P = 0.6$ [5] and the molecular diffusivity for PCP at very dilute concentrations was estimated to be $D_{AB} = 6.89 \times 10^{-6}$ cm^2/s. The tortuosity factor was estimated to be 1.4. This value indicates that the pores in ACF are more straight than in GAC since the tortuosity values in GAC generally fall between 2 and 5 [6].

Conclusions

The experimental concentration decay data was interpreted reasonably well by the diffusional model. The overall rate of adsorption of PCP onto ACF is predominantly controlled by the intraparticular diffusion that is exclusively due to pore volume diffusion. The external mass transport is much faster than the intraparticle diffusion, thus the external mass transfer resistance can be considered negligible.

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