

The Kinetics of Pentachlorophenol Adsorption onto Powdered Activated Carbon

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Introduction

The incorrect handling and disorderly application of pesticides can cause serious problems to the ecosystems and their components; among these are damage to vegetation and wildlife, and pollution to underground, surface, continental and coastal waters. Several processes have been developed to remove organic compounds from aqueous solutions. These processes can be classified into physicochemical and biological. Activated carbon adsorption, chemical oxidation and thermal oxidation are among the most important physicochemical processes. In biological processes the organic compound is biodegraded into inert substances; however, some very toxic organic compounds can not be biodegraded efficiently. These compounds are known as recalcitrant or resistant to biodegradation.

In the last 30 years, the adsorption on activated carbon has been used successfully for the treatment of municipal and industrial wastewaters as well as drinking water and it is considered the best available technology to eliminate organic non biodegradable and toxic compound present in aqueous solution [1].

Several studies have been carried out about the adsorption of PCP on various granular activated carbons (GAC) prepared from bituminous coal, pinewood, coconut shell, peach stones and *Eucalyptus globulus* chips [2-4]. These studies revealed that the PCP can adsorbed considerably on GAC and that the adsorption capacity of GAC is dependent on solution pH and temperature and GAC surface properties. Mollah et al. [5] investigated the adsorption rate of PCP in a GAC and assumed that the surface or solid diffusion was the only intraparticle diffusion mechanism.

The adsorption rate of organic compounds in porous activated carbons is mainly controlled by intraparticle diffusion [6]. It is expected that the adsorption rate of PCP in PAC is much faster than that of PCP in GAC since the particle diameters of PAC (0.015 to 0.025 mm) are around 100 times smaller than the particle diameters of GAC (1 to 3 mm); however, the adsorption rate of PCP in PAC has not been studied.

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

Diffusional model

The overall rate of adsorption in a porous adsorbent can be described by a mechanism of three consecutive steps: 1) external mass transport, 2) intraparticle diffusion and 3) adsorption at an interior site. Moreover, intraparticle diffusion 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 PAC. The model was derived assuming that intraparticle diffusion is solely due to pore volume diffusion. 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. The model equations were reported in a previous work [7].

Experimental

The PAC used in this work is commercially known as BM and is manufactured by Clarimex S. A. from a bituminous coal. The PAC was washed several times with distilled water and dried in an oven at 120 °C for 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.

The experimental batch adsorber used to obtain the adsorption isotherm data consisted of a 500 or 1000 mL Erlenmeyer flask. The batch adsorber containing the PCP solution, the PAC and a Teflon coated magnetic stirring bar, was partially immersed into a constant temperature water bath and set atop a magnetic stirrer to mix the adsorber solution.

The experimental data for the adsorption isotherm was obtained in the batch adsorber as follows. A predetermined mass of PAC was contacted with a fixed volume of a PCP solution of known initial concentration. The PCP solution remained in contact with the PAC until equilibrium was reached, which took place in 1 to 2 days. The solution pH was adjusted and kept constant at pH = 12 by adding 0.01 M HNO₃ solution. The solution was sampled at certain time intervals and the PCP concentration was determined for each sample. The PAC suspended in the solution must be removed during sampling. The solution was filtered using a cellulose acetate membrane placed in a filter holder which was connected to a vacuum pump. Equilibrium was reached when the PCP

concentration of two consecutive samples did not change and the amount of PCP adsorbed was calculated by performing a mass balance.

A continuous-stirred batch adsorber was used to carry out the rate of diffusion experiments. The adsorber was stirred by an impeller and was equipped with a glass coil to keep the temperature of the adsorption solution constant. The temperature and pH of the solution were measured periodically by means of a thermometer and a pHmeter. The adsorber solution was sampled by filtering the solution through a cellulose acetate membrane which was held in the bottom of the adsorber.

A certain mass of PAC and 975 mL of a buffer solution were poured into the adsorber. Then the motor of the stirrer was turned on. The PAC and the solution were continuously stirred and 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 20 mL of a solution of known concentration of PCF was added rapidly and the timer was turned on immediately. The adsorber solution was sampled periodically and the volume of the adsorber solution was kept constant by adding to the adsorber 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 adsorber 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:

$$\phi = \frac{C_A}{C_{A0}} \quad (1)$$

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 PAC was fitted to the adsorption isotherm model of Prausnitz-Radke, this model is represented by the following equation:

$$q = \frac{aC}{1 + bC^\beta} \quad (2)$$

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.

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 [8]. 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:

$$\Sigma(\phi_{\text{exp}} - \phi_{\text{pred}})^2 \quad (3)$$

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 two experiments. As it is shown in Figure 2, the diffusional model predicted reasonably well the experimental concentration decay data of the two experiments.

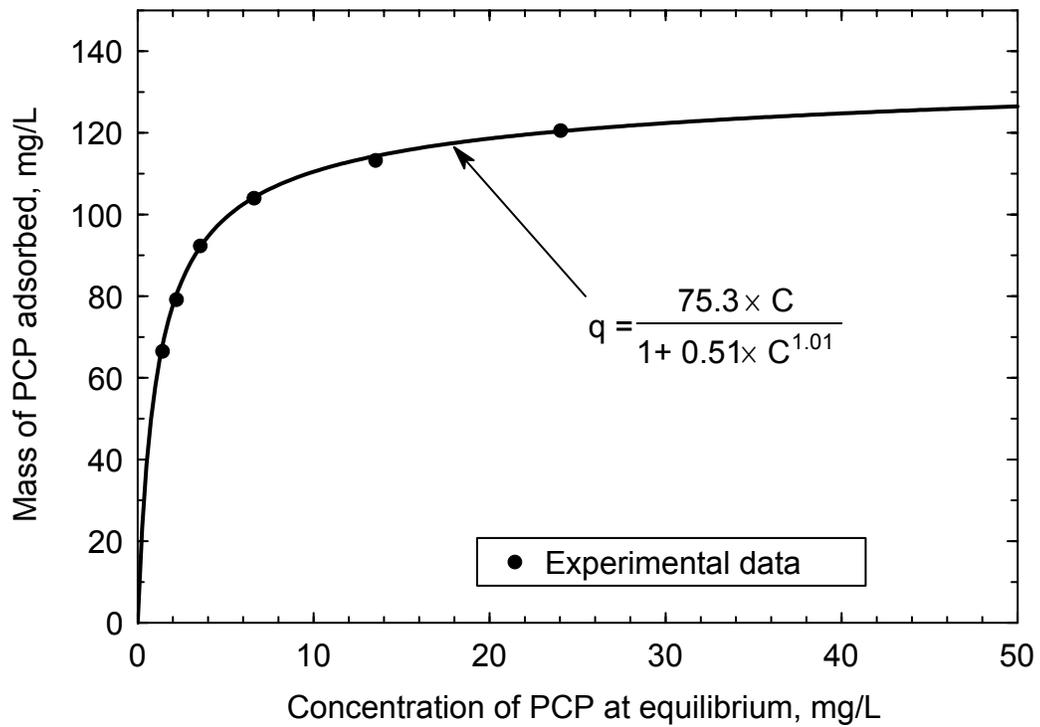


Figure 1. Adsorption isotherm of PCP on PAC.

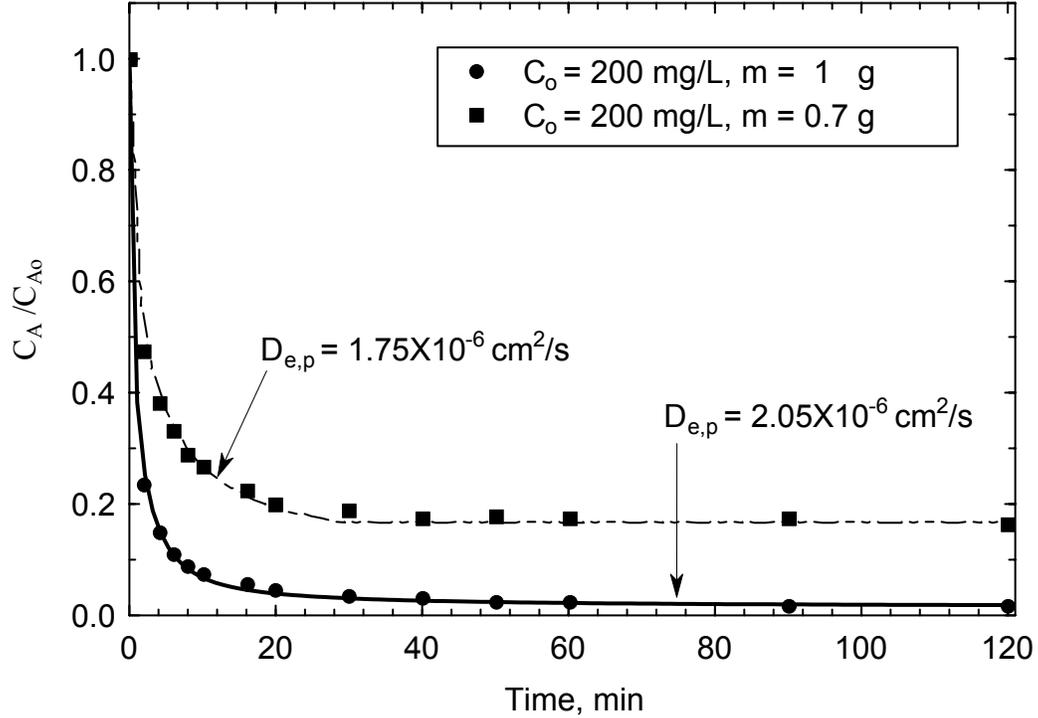


Figure 2. Concentration decay curve for PCP adsorption on PAC. The lines represent the diffusional model predictions.

The experimental values of the effective pore volume diffusivity for PCP varied from 1.45×10^{-6} and 2.5×10^{-6} cm^2/s . These values can be used to evaluate the tortuosity factor, τ_p , of carbon BM using the following equation [6]:

$$D_{e,p} = \frac{\epsilon_p D_{AB}}{\tau_p} \quad (4)$$

The molecular diffusivity for PCP at very dilute concentrations was estimated to be $D_{AB} = 6.89 \times 10^{-6}$ cm^2/s using the Wilke and Chang correlation [9] and the void fraction for this carbon is $\epsilon_p = 0.75$ [10]. The values of the tortuosity factor estimated using the above equation varied from 2.1 and 3.6. Leyva-Ramos and Geankoplis [6] suggested that the tortuosity factor of activated carbon can be assumed to be 3.5, this value is within the range of values for the tortuosity factor reported in this work.

Conclusions

The value of the effective pore volume diffusivity obtained by matching the experimental concentration decay data by means of the diffusional model, is very close to the value predicted using the molecular diffusivity, and the void fraction

and the tortuosity factor of the activated carbon. The experimental concentration decay data was interpreted reasonably well by the diffusional model.

The overall rate of adsorption of PCP onto PAC is predominantly controlled by the intraparticle diffusion that is exclusively due to the pore volume diffusion. The external mass transport is much faster than the intraparticle diffusion, thus the external mass transfer resistance can be considered negligible.

The effective pore volume diffusivity of PCP into PAC particles can be adequately predicted with the model that includes molecular diffusivity, and the void fraction and tortuosity factor of the carbon.

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