Hindered Diffusion of Asphaltenes at Evasluated Temperature and Pressure

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Abstract

During this time period, experiments were performed to study the diffusion controlled uptake of quinoline and a coal asphaltene into porous carbon catalyst pellets. Cyclohexane and toluene were used as solvents for quinoline and the coal asphaltene respectively. The experiments were performed at 27^{o}C and 75^{o}C, at a pressure of 250 psi (inert gas) for the quinoline/cyclohexane system. For the coal asphaltene/toluene system, experiments were performed at 27^{o}C, also at a pressure of 250 psi. These experiments were performed in a 20 cm^3 microautoclave, the use of which is advantageous since it is economical from both a chemical procurement and waste disposal standpoint due to the small quantities of solvents and catalysts used. A C++ program was written to simulate data using a mathematical model which incorporated both diffusional and adsorption mechanisms. The simulation results showed that the mathematical model satisfactorily fitted the adsorptive diffusion of quinoline and the coal asphaltene onto a porous activated carbon. For the quinoline/cyclohexane system, the adsorption constant decreased with an increase in temperature. The adsorption constant for the coal asphaltene/toluene system at 27^{o}C was found to be much higher than that of the quinoline/cyclohexane system at the same temperature. Apparently the coal asphaltenes have a much greater affinity for the surface of the carbon catalyst than is evidenced by the quinoline molecule.

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OBJECTIVES

1. To investigate the hindered diffusion of model compounds and asphaltenes in porous catalysts.

2. To examine the effects of temperature on the intraparticle diffusivity of model compounds and asphaltenes.

EXECUTIVE SUMMARY

This project aims to get a better understanding of the hindered diffusion of model compounds and asphaltenes in porous catalysts at various temperatures. In our work to date on the adsorptive diffusion of asphaltenes and other solutes in catalyst particles, the catalyst substrate utilized has been that of gamma *alumina*. This catalyst support is generally the most widely used in the oil and synthetic fuels industry, due to its economical cost and its good physical properties—high surface area and good mechanical strength. On the other hand, it has been found that one disadvantage of alumina as a catalyst support is the high coking rate, especially in coal liquefaction reactions. This coke formation leads to catalyst deactivation, sometimes, very rapidly, as a result of pore clogging and a decrease in pore surface area. This factor has led investigators to increased interest in other supports which may not be as susceptible to coking as the alumina. One of the most interesting of these porous supports is carbon. The pore structure of carbon supports is varied but the pore sizes are often somewhat smaller than aluminas, and can have a quite wide distribution. Therefore, during this time period we have examined the diffusion of asphaltenes and a model solute, quinoline, in a porous carbon. While several investigators have considered porous carbon as a potential catalyst support, and have examined it from the reactivity/activity standpoint, little detailed work has been done using porous carbon as a substrate for asphaltene diffusion studies. On the other hand there has been a considerable body of work performed in the water treatment field using porous, activated carbons, to remove substances from

the water. This removal process is an adsorption-diffusion process not unlike the analogous situation which occurs in the catalytic reaction field of interest in our work. For this reason, during the current time period, we made a detailed literature review of work done in the area regarding the diffusional controlled adsorption of substances on porous carbon. The results of this detailed literature review are presented in a following section of this report.

Also during the current time period, experiments were performed at 27^{o}C and 75^{o}C, at a pressure of 250 psi for the model compound quinoline with cyclohexane as solvent , and at 27^{o}C and 250 psi for a coal asphaltene with toluene as solvent. A program was written in C++ to simulate data using a mathematical model which incorporated diffusion and adsorption mechanisms. The simulation results for the diffusion controlled adsorptive uptake process showed that the mathematical model satisfactorily fitted the adsorptive diffusion of quinoline and the coal asphaltene onto porous carbon. In keeping with theories of adsorption, for the quinoline/cyclohexane system, the adsorption constant decreased with increase in temperature. The adsorption constant for the coal asphaltene/toluene system at 27^{o}C was much higher than that of the quinoline/cyclohexane system at the same temperature, giving an indication that the coal asphaltenes have a much greater affinity for the surface of the activated carbon catalyst than is evidenced by the quinoline molecules. The exact value of this parameter however is sensitive to the intraparticle diffusivity, which is based on estimated values of average properties such as pore diameter and asphaltene molecular size.

INTRODUCTION

Chemical reactions in heterogeneous catalysis can be significantly influenced by intrapore diffusion phenomena involved in the transport of reactant molecules in and out of the catalyst pores, resulting in the dependence of catalyst activity, selectivity and stability on intrapore diffusional limitations. However, the intrapore diffusion mechanisms are not yet fully understood. In the previous time periods, as noted in our previous project reports, Mr. Surya Vadlamani, who recently obtained his M.S. degree performing research on this project, had studied the effect of temperature and solvent composition on the diffusion controlled adsorptive uptake of model compounds and asphaltenes in a porous *alumina* catalyst. As noted in the executive summary, there is considerable interest in development of catalysts based on utilizing porous carbon, rather than alumina, as a catalyst support. Therefore, attention during the current time period has been focused on using this alternative material as a substrate for the diffusion studies. A study with porous carbon, which has a different range of pore sizes as well as surface properties, as compared to the alumina, would help us to more fully investigate the relationship between porous media properties and asphaltene diffusion into the catalyst pores. Thus, in the current time period, experiments were performed to study the diffusion controlled adsorptive uptake of quinoline in cyclohexane, and a coal asphaltene (C-257K) in toluene, onto a porous carbon. The effect of temperature and amount of the catalyst on the adsorptive uptake were also investigated for the quinoline/cyclohexane system.

LITERATURE REVIEW

Diffusional limitations can be an important factor in the overall speed of catalytic reactions. Hindered or restricted diffusion occurs when the sizes of the diffusing molecules are comparable to the pore sizes of the catalysts. In hindered diffusion regimes, the diffusion rates and the effective diffusivities of the molecules within the pores can be much smaller compared to those within the free solution. Thus this subject has been the object of considerable research. As a result, it has become widely accepted that hindered diffusion in the pores of the catalysts is caused by two important factors, steric partition effects and viscous drag influence. The steric hindrance or partition effect was first proposed by Ferry (1936) with regard to diffusion in membranes, rather than catalysts. Steric effects account for the fact that the diffusing molecules can enter a pore only if they do not strike the wall of the pore. This effect means that a small region near the wall of the pore is not accessible to the molecule. If the molecule is a sphere, this region is a distance equal to the molecule radius, for example. Viscous drag deals with the fact that the molecules experience an increased frictional drag (hydrodynamic resistance) due to the confinement of the fluid by the pore wall, over and above the drag that would be experienced had they been diffusing in an unconfined solvent (Deen, 1987). One might imagine a ball falling through a fluid confined in a pipe as an example of this effect. When the diffusing molecules adsorb on the pore walls, as is the case in most heterogeneous catalytic processes, a solute adsorption layer would further enhance the steric and hydrodynamic effects and additionally hinder the diffusion process. This effect has been discussed in a previous investigation performed in our laboratory by X. Yang as part of his PhD research (Yang,1997).

A comprehensive theoretical analysis of hindered diffusion was conducted by Anderson and Quinn (1974) and many applications of theories of hindered transport through membranes were reviewed by Deen (1987). In these investigations, a widely used relation is the molecular diffusivity as given by the Stokes Einstein equation

$$D_\infty = kT/6\pi\eta r_m \qquad (1)$$

where D_∞ is the molecular diffusivity, k is the Boltzmann constant, T is the temperature, η is the viscosity and r_m is the solute molecular size. In the catalyst pores, this diffusivity is reduced by several factors to give an effective pore diffusivity as,

$$D_e = K_p K_r \varepsilon D_\infty/\tau \qquad (2)$$

where K_p is the steric factor, K_r is the drag factor, ε is the porosity and τ is the tortuosity. The steric factor was examined by Ferry (1936) who postulated that

$$K_p = (1-\lambda)^2 \qquad (3)$$

where λ is the ratio of molecular size to pore size. Pappenheimer et al. (1951) gave the following relation to estimate the drag factor

$$K_r = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5 \qquad (4)$$

Equations (3) and (4) above are used in our work to provide estimates of the effective diffusivity of asphaltenes and other solute molecules in catalyst pores, as a funtion of the ratio of molecule to pore size. In a porous medium such as the porous carbon used in this time period, there is a wide distribution of pore sizes, and an average value must be used to extimate these factors. In addition the asphaltenes themselves have a distribution of sizes (Yang, 1997), and again an average size must be used to represent a hypothetical asphaltene molecule.

Our work seeks to examine the intraparticle diffusivity of the species existing in crude oils and synthetic liquids known as asphaltenes. Asphaltenes are a solubility class of compounds found in the original crude which are characterized by a high heteroatom content and a macromolecular colloidal nature (Ravikumar et.al., 1997). They are soluble in aromatic hydrocarbons, such as benzene or toluene, but insoluble in certain paraffins, such as pentane or hexane. Thus, the characteristics of one asphaltene may be somewhat different from that of another, depending on the origin from which it is derived and the exact operational procedure through which it is obtained. The term 'asphaltene' was originally used to denote a heavier petroleum sub-fraction, but now has been extended to describe similar fractions of materials derived from coal, oil shale, or other sources. Asphaltenes are thus described by an operational solubility classification, rather than a detailed set of chemical criteria. This fact makes it somewhat difficult to make exact calculations involved in the reactions of asphaltenes, and they are usually described by average or lumped properties such as average molecular weights, or average hypothetical structures, which may or may not represent the exact composition of the mixtures.

Review of Adsorption-Diffusion Studies using Porous Active Carbons

As noted earlier, in our work to date on the adsorptive diffusion of asphaltenes and other solutes in catalyst particles, the catalyst substrate utilized has been that of gamma *alumina*, while in the current time period the emphasis has been on utilizing a porous carbon catalyst as the substrate for the diffusion studies. As a result of the widespread utilization of porous activated carbons in the water treatment field there have been extensive studies concerning the adsorptive uptake of organic materials, often referred to as humic substances on porous activated carbons. These substances are naturally occurring organic materials consisting of decomposition products from plant and animal materials in the environment. They are generally high molecular weight materials with possibly charged molecules. For potable drinking water, it is necessary that these materials be removed, as is sometimes accomplished by active carbon adsorption. For example, the rate of humic substance uptake during activated carbon adsorption was studied by Summers and Roberts (1987) with a differential column batch reactor. Their experimental data was simulated by both pore and surface diffusion models to determine their appropriateness for representation of humic substance adsorption by activated carbon. They concluded that the interpretation of rate studies on the adsorption of humic substances by activated carbon is a rather difficult challenge for the following three reasons:

1) Macromolecular adsorption of the complex humic materials occurs by a very complicated mechanism.

2) Heterogeneity of the humic material complicates the exact assessment of their diffusional properties such as molecule sizes, etc. In fact, the diffusion coefficient of humic material is an average property of a wide range of molecular sizes.

3) A significant portion of the adsorbent’s (activated carbon) pore volume consists of pores which are smaller than the adsorbing molecules.

It is quite interesting that each of the above statements could also be made with regard to the adsorptive uptake of asphaltenes on the pores of catalysts as the asphaltenes are also a complex range of ill-defined materials, similar to the humic substances noted above. A couple of other complicating factors are that the size of the adsorbing humic molecules corresponds to the lower end of the adsorbent’s mesopore size range and finally, when the solution concentration is reduced, sometimes little or no desorption of humic substances is observed. As a result of a comparison of experimental data with model predictions of the uptake of humic substances, it has been noticed that the fit between the data and the model prediction becomes increasingly inaccurate as the system approaches equilibrium, i. e., at longer times. Many times, it is found that the models need a large diffusion coefficient to fit the data during the initial stages of the uptake, but this large diffusivity overestimates the uptake rate during the latter stages. To solve this problem, one could approximate the latter stages by decreasing the diffusivity, but that would be at the cost of accuracy during the initial stages of the uptake. Another way to approach this problem is to utilize a so-called two-domain model for the porous substance, in this case active carbon. For the two-domain model, it is supposed that the porous material is actually made of an assembly of smaller microparticles. The diffusivities in the macropores of the composite material are thought to be larger than those in the micropores of each microparticle. This approach gives two time scales in modeling the uptake process, and is better able to represent the experimental data; however, it suffers from the disadvantage that generally the properties of the "microparticles" are not well known. Of course, single-domain diffusion models can be used quite well to simulate the initial stages of the uptake. As a result of their investigation, Summers and Roberts (1987) concluded that a two-domain diffusion model with hindered diffusion in macropores and mesopores controlled the initial stages of adsorption, while the latter stages were controlled by more stronger hindered micropore diffusion. It is interesting that some of our own data taken during this time period also show a more rapid uptake in the initial phase of the adsorption, with a slower rate during the later phases. A two domain type model might be employed for asphaltene diffusion in these cases with some advantage.

Generally, most of the models for fixed bed carbon adsorbers have used either a homogeneous solid diffusion model (HSDM) or a pore diffusion model (Weber and Chakravorti, 1974). The two models lead to more or less the same breakthrough curves for the bed when the adsorption isotherm is linear. Hence, the choice of models has not been critical in many studies where the isotherm was almost linear. But, in the case of a nonlinear isotherm, the choice of model becomes more important. The HSDM assumes that transport within the adsorbent particle is limited by surface diffusion and that this can be described by an overall constant surface diffusion coefficient. The pore surface diffusion model clearly distinguishes the pore and surface diffusion mechanisms. It is sometimes recommended for bed design that a number of batch tests be performed and then by comparing the experimental rates of adsorption with those predicted by the two models, the appropriate model can be selected. In the case of the pore diffusion model, the porosity factor is very important, especially at low porosity values. As is assumed in our own work, both of these commonly used models (pore surface diffusion model and homogeneous surface diffusion model) generally assume that the adsorption step at the adsorbent surface is very fast and hence the rate limiting step is diffusion. During the latter stages of the adsorption-diffusion of macromolecules, it is possible that this assumption might not be valid. Using a variety of model solutes, Mathews and Weber (1984) have reviewed several models which have been proposed for the adsorption mechanism. They have also looked at the homogeneous solid phase diffusion model in depth for predicting adsorption rates in slurry reactors. Model verification was done using experimental data for four different solutes (phenol, p-bromophenol, dodecyl benzene sulfonate and p-toluene sulfonate). These researchers found that the equilibrium loadings on the solid phase for phenol and p-bromophenol were an order of magnitude greater than those for p-toluene sulfonate and dodecyl benzene sulfonate. Dodecyl benzene sulfonate is a large molecule with a diffusion coefficient much lower than that of phenol, p-bromophenol and p-toluene sulfonate. Hence, the study used two solutes with high equilibrium loadings and big diffusion coefficients, one solute with low loading and big diffusion coefficient, and one solute with low loading and a comparatively low diffusion coefficient. In their study, they have also developed a parameter estimation program to estimate the external mass transfer coefficient and the solid phase diffusion coefficient from batch reactor rate data

In another model compound study, aqueous solutions of benzene with activated carbon particles in agitated, baffled vessels were used to study the adsorption of benzene (Furusawa and Smith, 1973). The effects of stirrer speed and particle size on the fluid-particle mass transfer coefficient were studied. The transport coefficients measured in these slurry adsorbers were found to be in agreement with those obtained by dissolution of nonporous particles in agitated vessels. The study suggested the presence of significant intraparticle diffusion resistance. These researchers also concluded that surface diffusion was responsible for the high values of effective diffusivities in the liquid-filled pores. Levya-Ramos and Geankoplis (1985) have developed a mathematical model for solute adsorption rates by porous solids. The model considers the various mass transfer resistances and nonlinear isotherms.

The Freundlich isotherm is:

$$q = KC_r^{1/n} \tag{5}$$

where:

q = mass of solute adsorbed per unit mass of adsorbent

K = adsorption constant

C_r = concentration of solute in the pore volume at a radial position r

r = the distance in radial coordinate direction inside the particle

Several calculations using this isotherm were used to study the model and to make numerical and graphical parametric studies. For activated carbon, typical values of n lay between 2 and 5. The Langmuir isotherm was not used since generally data were well correlated by either the Freundlich or the Langmuir isotherm. In the case of combined surface and pore diffusion, the overall rate of adsorption for a slightly adsorbing solute was significantly affected by the addition of surface diffusion to ordinary pore diffusion. For a highly adsorbing solute, adding surface diffusion to pore diffusion affected the overall rate of adsorption even more. Levya-Ramos and Geankoplis, (1985) also found that for a slightly adsorbing solute, the rate of adsorption was controlled by the external mass transfer coefficient (k) for values of k below 0.0001m/s. When k increased beyond 0.0001m/s, there was no increase in the rate of adsorption and at that point pore or pore plus surface diffusion was the rate determining mechanism. One interesting observation which occurred was that, for a slightly adsorbing solute, after a very short time, the concentration at the pore mouth was above the final equilibrium concentration because the external mass transfer provided more solute than that which could be removed by adsorption and diffusion in the pore. On the contrary, for a highly adsorbing solute, the concentration at the pore mouth was always below the final equilibrium value. This happened as a result of the fact that the pore surface readily adsorbed the solute and allowed it to diffuse away rapidly by both surface and pore diffusion.

In another adsorption-diffusion study, Neretnieks (1976) proposed a method to determine transport coefficients from finite bath adsorption experiments. The method was based on models describing the diffusion in the solids. He investigated six different model compound adsorption systems (the adsorbed components were phenol, parachlorophenol, phenylacetic acid, benzoic acid, paranitrophenol and 2,4-dichlorophenoxyacetic acid). He found that surface diffusion governed the transport mechanism in all the cases. In some cases, the diffusion coefficient is a constant, however, the bonding energy changes with concentration for many systems, especially for those having a strong nonlinear isotherm. A concentration dependent coefficient of surface diffusion can be expected for such systems. Neretnieks also found that for quite a few systems, the Freundlich isotherm did not fit the data very well. In order to get a better fit of data over a wide range, the modified Temkin isotherm was used. The Temkin isotherm is based on the assumption that the heat of adsorption decreases linearly with increasing concentration. Neretnieks also tried to separate the individual contributions from pore and surface diffusion, but the attempt was not very successful.

Ruckenstein (1971) studied adsorption by solids with bidisperse (bimodal) pore structures. In solids with bidisperse pore size distributions, diffusion and adsorption occur simultaneously in both the micropores and the macropores and these competing effects have to be taken into consideration when developing a model. Diffusion limited sorption occurs in both the micropores and the macropores of the bidisperse solid. We have already discussed this above when referring to the single and two-domain type models for adsorption and diffusion. Along these lines, Ruckenstein (1971) developed a two domain model for sorption rate which considered a spherical macroporous sorbent particle to be made up of an assembly of small microporous spheres. In developing the model, he made the assumptions that the sorption process was isothermal and that adsorption is described by linear isotherms. He also assumed the bath concentration to be constant, instead of being a function of time, as is the case in our work. These assumptions gave a somewhat simpler mathematical treatment. He has also suggested that a good method to determine the relative importance of micropore and macropore diffusion is to conduct experiments where both the macrosphere and microsphere sizes are varied. A more detailed treatment with the time dependent bath concentration being considered has been made by Ma and Lee (1976) and Lee (1978).

While our own experiments are performed in a batch mode, uptake experiments using porous active carbon have been conducted in both batch and continuous (fixed bed) configurations. For example, Cornel et al. (1985) measured the external mass transfer coefficients for fixed bed activated carbon adsorption of paranitrophenol and 2,4-dichlorophenol. The experimental values of the external mass transfer coefficients were then compared with values which were predicted from four mass transfer correlations (correlations developed by Williamson et al.; Wilson and Geankoplis; Gnielinski; and Ohashi et al.). The correlation by Gnielinski was found to give the closest prediction to experimental values. But, the observed values exceeded the predictions from correlations by a factor of 1.5 to 2. This might possibly be due to increased specific surface area due to adsorbent grain angularity and surface roughness. For this reason the use of a generalized correlation like the one by Gnielinski, with the requisite correction for particle shape, has been suggested as a method to model the external mass transfer in fixed bed granular activated carbon adsorbers. On the other hand, it has also been suggested that if the experimental values of external mass transfer coefficients are more than twice those predicted from the correlations, then the experiment should be reviewed for possible errors.

Lee et al. (1983) performed adsorption studies using a commercial humic acid, peat fulvic acid and a coagulated peat fulvic acid with both a completely mixed batch reactor and a fixed bed column. They evaluated the experimental data with a homogeneous surface diffusion model. The model was effective in simulating column data for four granular activated carbons (HD-3000 from ICI Americas Inc., Wilmongton, Del.; F-400 from Calgon Corporation, Pittsburg, Pa.; WV-G and WV-W from Westvaco, Covington, Va.) using column-determined surface diffusivities. However, the model was unable to predict column data using batch-determined surface diffusivities except for small adsorbent particles. The investigators suggested particle attrition in the batch tests to be the reason for this. Further, because the rate studies with humic substances were conducted for around 24-36 hours (as compared to the general 6-10 hour runs for other substances) more particle attrition could occur. Another possible source of difficulty was noted by Summers and Roberts (1987) who have suggested as an alternative reason that equilibrium was not fully attained for the large adsorbent particles due to possibly insufficient run periods which were less than 30 hours for the completely mixed batch reactors.

During the adsorption of a multicomponent material such as humic materials, or asphaltenes, for that matter, it is possible and indeed likely for one component to displace an already adsorbed component. Along these lines, Furusawa and Yamamoto (1983) have studied the displacement from the adsorption layer of a polymer by another for different molecular weight combinations of polystyrene using the technique of gel permeation chromatography. They observed that the low molecular weight polymers which were adsorbed earlier were extensively displaced by the larger molecules. This appears to agree with our own research which has shown increased adsorptivity for the higher molecular weight species (Yang, 1997). The degree of displacement of the previously adsorbed species was dependent on the difference in their molecular weights (the larger the difference in molecular weights, the greater was the exchange). The degree of displacement also depended on the solution concentrations at which adsorption was carried out. This latter phenomenon was difficult to explain although it was postulated that the polymer molecules in a dilute solution reached a more sparsely occupied surface and thus adopted a relatively flat and harder to displace conformation while polymer molecules in a concentrated solution, especially the later arrivals, reached a densely populated surface and were adsorbed in an extended loop conformation which could be displaced much more easily as compared to the flat conformation. This seems to be a reasonable speculation for the observations.

Cornel et.al. (1986) estimated the diffusion coefficients in aqueous solutions of polyethylene oxide (PEO), polystyrene sulfonate (PSS) and a commercial humic acid by making measurements of external mass transfer coefficients in a fixed bed activated carbon adsorber. The diffusivity of the PEO was determined to be independent of the ionic strength of the solution while the diffusivities of PSS and humic acid increased with increasing ionic strength of the solution. This was thought to be because PEO is a neutral macromolecule while PSS and humic acid are charged macromolecules and hence are supposed to become coiled as the ionic strength of the solution increases. Membrane filtration experiments also confirmed this as exemplified by the observation that PSS molecules which are rejected by a membrane at low ionic strength can pass the same membrane when the ionic strength of the solution increases. Similar observations were made for humic acid as well.

In a recent paper, Lyn (1996) studied adsorption on granular activated carbon in a completely mixed batch reactor in the near equilibrium regime with both the homogeneous surface diffusion model (HSDM) and the pore surface diffusion model (PSDM). Lyn points out several previously unrecognized features of the solutions of the HSDM and the PSDM which could be useful in deciding the experimental data to be taken for analysis as well as in the subsequent analysis of the data. For estimation of the external mass transfer coefficient, an asymptotic short-time solution can be used since initial transport is limited by external mass transfer and in this regime the short-time solution is valid. Lyn linearized the model equations and restricted his study to single solute systems and to systems for which the adsorption equilibrium could be described by a single set of isotherm parameters. The Freundlich isotherm was used in his work. Lyn verified his theoretical asymptotic analysis by numerical simulations of the model equations. He developed some techniques for evaluation of the importance of pore diffusion relative to surface diffusion using the near-equilibrium region. However in this region great care in chemical analysis is required since changes in concentration are small. In addition, at low initial and equilibrium concentrations, analytical problems may be greater due to instrumentation limitations and inaccuracies. Lyn has basically given a fairly simple method for determining diffusion coefficients from batch experiments and has pointed out the qualitative differences in the behavior of the solutions of the HSDM and the PSDM. These differences can be used in an assessment of the relative importance of the two diffusion mechanisms. Lyn has also illustrated his method by comparing the estimates obtained by the analysis of two data sets with those obtained by a more conventional method.

Ouki and Neufeld (1997) performed a study concerning the use of activated carbon for the recovery of chromium from industrial wastewaters. They concluded that adsorption and desorption of chromium on activated carbon are strongly dependent on the pH conditions. Alkaline regeneration recovered chromium in its hexavalent state while acid regeneration recovered it in its trivalent state. A combination of caustic followed by acid regeneration of the exhausted activated carbon bed maximized the recovery efficiency.

Knappe et.al. (1998) developed a method for predicting the capacity of powdered activated carbon for trace organic compounds in natural waters. Some of the advantages in using powdered activated carbon for drinking water treatment were found to be:

1) It can be fed in many drinking water treatment plants with a relatively small investment of capital.
2) It is cheaper than granular activated carbon.

In order to predict the removal of trace organic compounds from natural waters by powdered activated carbon, one needs to know both the equilibrium as well as kinetic parameters. The kinetic parameters which describe the rate of trace organic compound adsorption from natural waters can be obtained with the pseudo-single solute homogeneous surface diffusion model, although estimation of the competitive effect of background organic matter on the equilibrium parameters of trace organic compounds is difficult. In their study with powdered carbon these investigators used the model compounds, atrazine and 2-methyl-isoborneal. The ideal adsorbed solution theory was used for modeling competitive adsorption equilibria in their systems involving non-linearly adsorbing micropollutants and background organic matter. One simplification made however was that a single hypothetical compound, considered to be an equivalent background compound, was used to represent the competing background organic matter. In this manner, the more complex system was modeled as a bi-solute system, in which the two adsorbates were the trace organic compound and the equivalent background compound. The Freundlich adsorption isotherm was used in the ideal adsorbed solution theory. The analysis of experimental data and mathematical modeling results showed that the powdered activated carbon capacity for a micropollutant in natural water was proportional to the initial micropollutant concentration for any given amount of powdered activated carbon. This proportionality was observed even though nonlinear isotherms were obtained from experiments conducted with a given initial micropollutant concentration and varying amounts of powdered activated carbon. Their study illustrated the importance of background organic matter competition on the powdered activated carbon capacity for adsorption of solutes from in natural waters. Summing up, based on the analysis of the ideal adsorbed solution theory and the experimental data, the initial concentration dependence of the powdered activated carbon capacity for a trace organic compound in natural water could be estimated without the use of mathematical models provided the isotherm data were collected for a micropollutant at a single trace initial concentration in the natural water.

In another study on porous carbon diffusion-adsorption, Harding et.al. (1998) studied the adsorption and desorption kinetics of water vapor on two carbons with widely different pore structures as a function of relative pressure and temperature in order to understand the effect of changes in atmospheric conditions on the adsorption and desorption of water vapor. The dynamics of water vapor adsorption and desorption are very important for the characterization of carbon adsorbents as the presence of water vapor in air affects their performance. The kinetics of water vapor adsorption on carbon were found to follow the model

$$M_t/M_e = 1-e^{-kt} \tag{6}$$

where M_t is the uptake at time t, M_e is the equilibrium uptake and k is the rate constant.

Wilmanski and Breemen (1990) studied the competitive adsorption of trichloroethylene (TCE) and humic substances from groundwater on activated carbon. They performed comparative column experiments for the estimation of the TCE removal from water containing different total organic carbon concentrations but the same inorganic composition. As a result of their investigation, they concluded that natural organics in groundwater could significantly decrease the adsorption rate and activated carbon capacity for TCE. It is to be noted that there was no influence of TCE on the adsorption of humic substances.

Carter et.al. (1992) studied the effects of background dissolved organic matter and reactor configuration on TCE adsorption by granular activated carbon. Due to their large relative size, macromolecular components of dissolved organic matter reduced the capacity of granular activated carbon by pore blockage. Further, dissolved organic matter also was adsorbed on the carbon. Along these lines, we have found that similar pore blockage effects can reduce the rate of diffusion of asphaltenes into deactivated catalysts and catalysts with pre-adsorbed asphaltene components (Yang, 1997).

Kilduff et.al. (1998) studied the adsorption of TCE by granular activated carbon preloaded with humic substances. Generally speaking, it has been found that macromolecular dissolved organic matter reduces the efficiency of activated carbon adsorbers for removal of synthetic organic contaminants. There are two mechanisms thought to be operating in this reduction of efficiency. Initially, a reduction in granular activated carbon capacity for TCE adsorption is believed to be a result of competition with the humic substances for adsorption sites. But, at extended times, pore blockage, such as noted in the preceding study, is the primary factor which reduces the capacity. In the study by Kilduff et al., the effects of the molecular weights of preloaded humic and fulvic acids on the subsequent adsorption of TCE by activated carbon was studied in detail. TCE isotherms were measured on preloaded carbon in completely mixed batch reactors and compared with TCE adsorption on nonpreloaded carbon. The 2-parameter Freundlich and the 3-parameter Langmuir-Freundlich isotherms were used to model the TCE isotherms. The combined Langmuir-Freundlich isotherm is

$$q_e = Q\,(bC_e)^n / (1 + (bC_e)^n) \qquad (7)$$

where q_e is the amount adsorbed at equilibrium per unit mass of adsorbent, C_e is the equilibrium solution phase concentration and Q, b and n are empirically determined parameters. As a result of their investigation, Kilduff et al. (1998) concluded that the low molecular weight components of the humic solution most significantly reduced the adsorption of TCE. Further, even though there was a significant uptake of the higher molecular weight components, they did not compete effectively with TCE.

Garcia et.al. (1998) studied the adsorption of gallic, tannic and humic acids on activated carbon. The capacity of activated carbon to adsorb gallic acid was much higher than for the other two acids. This is due to the molecular size of the acids. Gallic acid has the lowest molecular size while humic acid has the largest. The micropores of the activated carbon are almost inaccessible to humic acid. A similar situation may exist with respect to some asphaltene macromolecules in relation to catalysts with partially accessible pore structures.

Experimental Section

Materials

In the model compound adsorptive diffusion experiments which were conducted during this time period, quinoline (Fisher Scientific) was used as the solute and cyclohexane (also from Fisher Scientific) was the solvent. For the coal asphaltene/toluene system, the asphaltene utilized was termed C-257K (obtained from the Wilsonville Advanced Coal Liquefaction Research and Development Facility, Wilsonville, Alabama) while toluene (Fisher Scientific) was the solvent. The properties of coal asphaltene C-257K have been given in our previous reports on this project and also by Yang (1997). For both the systems, the same porous activated carbon catalyst, with an irregular shape, an equivalent particle radius of 0.2 cm and a surface area of 1100 m^2/g was used as the adsorption-diffusion medium. Table 1 contains additional properties of the porous carbon catalyst. A pore size distribution for the catalyst is shown in Figure 1. From this figure, it can be observed that the pore size distribution is very broad with a wide range of macro and meso pores.

Apparatus and Procedures

1. Quinoline/Cyclohexane system

The adsorptive uptake of quinoline in cyclohexane on porous activated carbon at 27^oC was performed in a microautoclave batch reactor where the porous carbon particles, presoaked in cyclohexane, were supported in a wire mesh compartment to avoid direct contact with the solution until the experiment was begun. The microautoclave was purged with helium 5 times to remove air from the system and was left pressurized to 250 psig with helium for the duration of the experiment. The microautoclave was attached to a horizontal agitator and runs were made for various time periods with an initial quinoline concentration corresponding to 270 ng N/μL. After a run, the liquid phase was collected, filtered and then analyzed with a Dohrmann nitrogen analyzer to determine the quinoline concentration in the liquid phase after the diffusional uptake experiments.

Similar experiments were conducted at an elevated temperature of 75°C in which the microautoclave was lowered into a fluidized sand bath whose temperature was maintained at 75°C by a temperature controller. The runs were made for various time periods with an initial quinoline concentration corresponding to 0.02256 g/L of solution. After a run, the liquid phase was collected, filtered and then analyzed with a UV spectrophotometer at 269.3 nm to determine the quinoline concentration in the liquid phase after the uptake experiments.

2. Coal asphaltene/toluene experimental system

In the experiments using actual coal asphaltenes, the basic procedure remained the same as above except for the fact that the solute is now coal asphaltene denoted as C-257K and the solvent is toluene. The initial concentration of asphaltene C-257K was 0.05g/L of solution. The experiments were performed at 27°C and analyses were made using a UV-VIS spectrophotometer at 400 nm to determine the C-257K concentration in the liquid phase after the uptake experiments.

RESULTS AND DISCUSSION

I Quinoline/Cyclohexane system

1. Effective and molecular diffusivities

a) Experiments at 27°C

In our earlier work, the radius of a quinoline molecule was extimated to be 3.45 x 10^{-8}cm (Yang, 1997). The viscosity of cyclohexane was determined to be 0.87 cP (Perry and Chilton, 1973) at the experimental temperature. The average pore diameter based on pore volume and surface area was obtained from the porous carbon properties and is recorded in Table 1. Using these values in equation (1), we find the value of molecular diffusivity D_∞ to be 7.317 x 10^{-6} cm^2/s. Then, using equation (3), we find that the steric hindrance factor K_p is estimated to be 0.582. Similarly, using equation (4), we find that K_r is 0.5283. The tortuosity values for activated porous carbons covers a range from about 1 to 10. Therefore it was decided to adopt an average value based on previous studies. Thus, from the literature, the tortuosity of activated carbon was estimated to be about 4 (Summers and Roberts, 1987). Using these values in equation (2), we estimate the value of the effective diffusivity D_e to be 3.49 x 10^{-7} cm^2/s at 27° C.

b) Experiments at 75°C

As before, allowing for the effect of temperature on viscosity, and then using equation (1), the value of D_∞ obtained is 2.05 x 10^{-5} cm^2/s. Using equation (2), we find the corresponding value of D_e to be 9.78 x 10^{-7} cm^2/s. The above values of estimated parameters are recorded in Tables 2-4.

2. Comparison of experimental data with mathematical model simulations

The experimental data obtained during adsorptive uptake experiments for the quinoline/cyclohexane system at 27^oC and 75^oC are given in Tables 5 and 6, respectively. The data in these tables was used to compare with the uptake simulated by the mathematical model for the diffusion-controlled uptake process as developed in our previous project reports. The results of the comparisons between experimental data and model simulations (curves) are presented in this section. In order to fit the model simulation to the experimental data least squares estimations were performed to select the best value of the adsorption equilibrium constant K which appears as a parameter in the mathematical model. Following this procedure, the experimental data for the quinoline/cyclohexane system at 27^oC for V=5ml and W=0.5g was compared with model simulations. The value of adsorption constant K which best fits the experimental data was found by least square analysis to be 2775 cc/g. Figure 2 shows the comparison between the experimental data and model simulations for three different values of K (2000, 2775 and 3500 cc/g). The curves are fairly close together, however, the value of 2775 has the best fit in the least squares sense. Using this value, Figures 3 and 4 show the comparison between the experimental data and model simulation for the best fit value of K. Figure 4 is an alternate method of plotting the results of the uptake experiment in terms of the approach to equilibrium based on the total amount of solute M_t taken up by the catalyst (adsorbed plus that in the pore volume liquid). This value is related to the concentration of solute in the bath by a simple solute material balance on the solute remaining in the well mixed fluid. Similar to the experiments at 27 ^{o}C, for the quinoline/cyclohexane system at 75^{o}C, the experimental data is compared with model simulations. The value of K which best fits the experimental data was found by least square analysis to be 625 cc/g. Figure 5 shows the comparison between the experimental data and model simulations for three different values of K (200, 625 and 1200 cc/g). Likewise, Figures 6 and 7 show the comparison between the experimental data and model simulation for the best fit value of K.

3. Adsorption Constant

From the comparisons between the mathematical model and the experimental data as given in the preceeding section, the value of the adsorption constant is 2775 for the quinoline/cyclohexane system at 27^{o}C. Similarly, at 75^{o}C, the value of the adsorption constant is 625. Table 8 records these values. The results in Table 8 show that, consistent with adsorption being an exothermic process, the values of adsorption equilibrium constant decline with increasing temperature. As shown in Table 8, at higher temperatures, the adsorption constant for the quinoline/cyclohexane system decreases very significantly. So, even though the molecular and effective diffusivity increases, the net adsorptive uptake decreases, as is shown in Figure 8.

4. Effect of amount of catalyst

An experiment to examine the effect of catalyst loading (W/V) was performed for the quinoline/cyclohexane system at 27°C, wherein the weight of the catalyst is decreased to 0.1g from 0.5g, keeping the volume of quinoline/cyclohexane solution constant at 5ml. These results are shown in Figure 9 where the uptake is seen to decrease as the catalyst loading is reduced. It can be seen that the model is consistent in that the same value of K is fitting the data at the new catalyst loading.

II Coal Asphaltene C-257K / Toluene system

In a second series of experiments during this time period, diffusional adsorption experiments were carried out using the carbon catalyst and a coal asphaltene with toluene as the solvent. Experimental data from these experiments are compared with the simulation results from the mathematical model in the following sections.

1. Effective and molecular diffusivities

The molecular weight of coal asphaltene C-257K is estimated from our previously reported work to be 490 (Yang, 1997). Also from the previous work on this project, Yang (1997), we obtained a relation for the size of the coal asphaltene as a function of the molecular weight as:

$$r_m = 0.36\ M_s^{0.5} \qquad (8)$$

where M_s is the molecular weight of the asphaltene. From equation (8), the radius of the C-257K molecule is determined to be 7.97×10^{-8} cm. At the experimental temperature of 27°C, the viscosity of toluene is 0.55 cP (Perry and Chilton, 1973).

Using these values and the average pore radius in Table 1 in equation (1), we obtain the value of molecular diffusivity D_∞ to be 5.01 x 10^{-6} cm^2/s. Now, using equation (3), we find that the steric factor K_p is 0.2045 and from equation (4), we find that the hydrodynamic factor K_r is 0.1441. These hindrance factors are quite low because of the small value of average pore diameter for the porous carbon catalysts. Based on these values, we expect the diffusional uptake of asphaltenes into the porous carbon to be significantly hindered. Using these values in equation (2), we find the value of effective diffusivity D_e to be 2.29 x 10^{-8} cm^2/s.

2. Comparison of experimental data with model simulations

The experimental adsorptive uptake data for the coal asphaltene C-257K/toluene system at 27^{o}C is given in Table 7. The experimental data in the table is compared with model simulations in the following figures. Figure 10 shows the comparison between the experimental data and model simulations for three different values of K (2 x 10^5, 3.07 x 10^5 and 4 x 10^5 cc/g). The value of K which best fits the experimental data was found by least square analysis to be 3.07 x 10^5 cc/g. Figures 11 and 12 show the comparison between the experimental data and model simulation for the best fit value of K.

3. Adsorption Constant

For the coal asphaltene C-257K/toluene system at 27°C, the value of the adsorption constant was determined to be 3.07×10^5 cc/g. This is much higher than the adsorption constant values for the quinoline/cyclohexane system. Apparently the coal asphaltenes have a much greater affinity for the surface of the activated carbon catalyst than is evidenced by the quinoline molecule.

Table 1. Properties of Activated Carbon (Calgon Carbon's BPL 4 x 6)

Shape	Irregular
Equivalent radius, cm	0.2
Surface area, m^2/g	1100
Particle density, g/cm^3	0.8
Pore volume, cm^3/g	0.8
Porosity	0.62
Average pore diameter, nm	2.91

Table 2. Parameter values for the quinoline/cyclohexane system at 27°C

Viscosity[a]	0.87 cP
Molecular diffusivity[b]	7.317×10^{-6} cm^2/s
Effective diffusivity[c]	3.49×10^{-7} cm^2/s

(a) Obtained from Perry and Chilton (1973)

(b) Calculated from equation (1)

(c) Obtained from equation (2) assuming a tortuosity factor of 4.

Table 3. Parameter values for the quinoline/cyclohexane system at 75^{o}C

Viscosity(a)	0.36 cP
Molecular diffusivity(b)	2.0513 x 10^{-5} cm^{2}/s
Effective diffusivity(c)	9.78 x 10^{-7} cm^{2}/s

(a) Obtained from Perry and Chilton (1973)

(b) Calculated from equation (1)

(c) Obtained from equation (2) assuming a tortuosity factor of 4.

Table 4. Parameter values for the C-257K / toluene system at 27^{o}C

Viscosity(a)	0.55 cP
Molecular diffusivity(b)	5.01 x 10^{-6} cm^{2}/s
Effective diffusivity(c)	2.29 x 10^{-8} cm^{2}/s

(a) Obtained from Perry and Chilton (1973)

(b) Calculated from equation (1)

(c) Obtained from equation (2) assuming a tortuosity factor of 4.

Table 5. Experimental data for the quinoline/cyclohexane system at 27^{o}C

V = 5ml W = 0.5g			V = 5ml W = 0.1g		
Time, hr	C_b/C_i	M_t/M_{eq}	Time, hr	C_b/C_i	M_t/M_{eq}
0	1	0	0	1	0
0.25	0.334	0.669	0.25	0.753	0.251
0.5	0.244	0.759	0.5	0.66	0.346
1	0.181	0.822	1	0.545	0.463
1.5	0.128	0.875	1.5	0.483	0.526
2.5	0.08	0.923	2.5	0.409	0.602
3	0.075	0.928	3	0.385	0.626

Table 6. Experimental data for the quinoline/cyclohexane system at 75°C (V=10ml, W=1g)

Time, hr	C_b/C_i	M_t/M_{eq}
0	1	0
0.25	0.339	0.671
0.5	0.265	0.746
1	0.224	0.789
1.5	0.207	0.806
2.5	0.165	0.848
3	0.156	0.857

Table 7. Experimental data for the C-257K / toluene system at 75°C (V=10ml, W=1g)

Time, hr	C_b/C_i	M_t/M_{eq}
0	1	0
0.5	0.591	0.409
1	0.503	0.497
1.5	0.429	0.571
2	0.37	0.63
2.5	0.326	0.674
3	0.298	0.702

Table 8. Adsorption constant values

System	Temperature (^oC)	Adsorption Constant (cc/g)
Quinoline/Cyclohexane	27	2775
Quinoline/Cyclohexane	75	625
C-257K / toluene	27	3.07×10^5

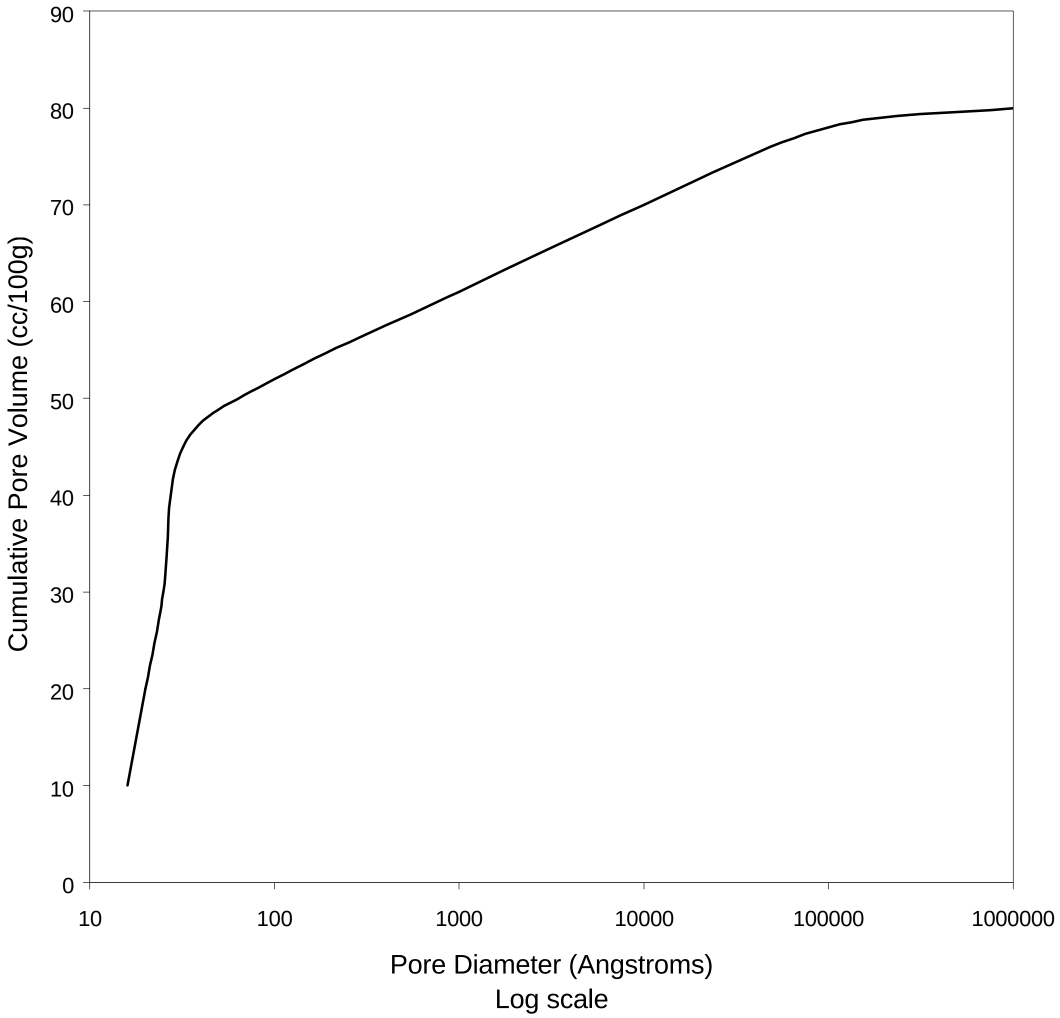

Figure 1. Pore Size Distribution of Calgon Carbon's BPL 4 x 6 porous carbon (from Product Bulletin of Calgon Carbon,1997)

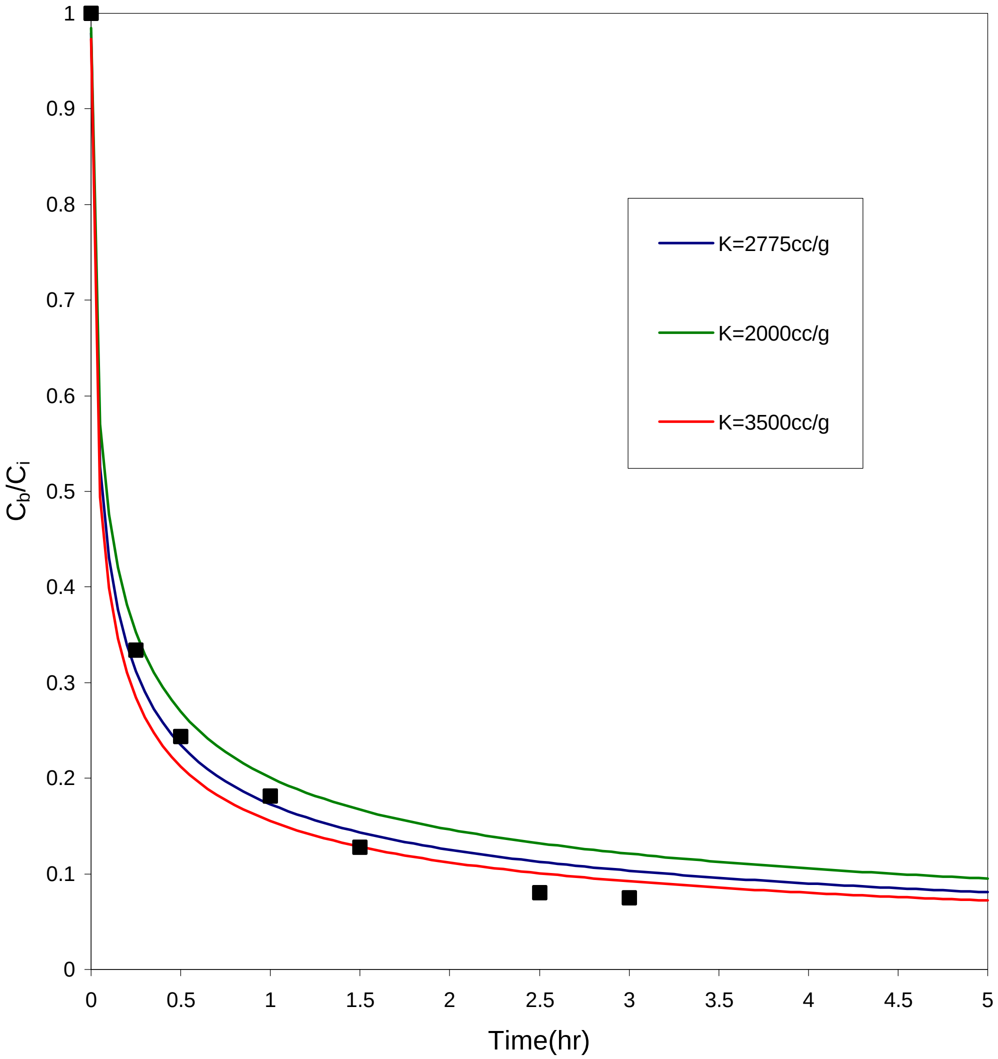

Figure 2. Comparison between experimental data and model simulation for the adsorptive uptake of quinoline in cyclohexane on porous carbon catalyst (V=5ml, W=0.5g, T=27^{o}C)

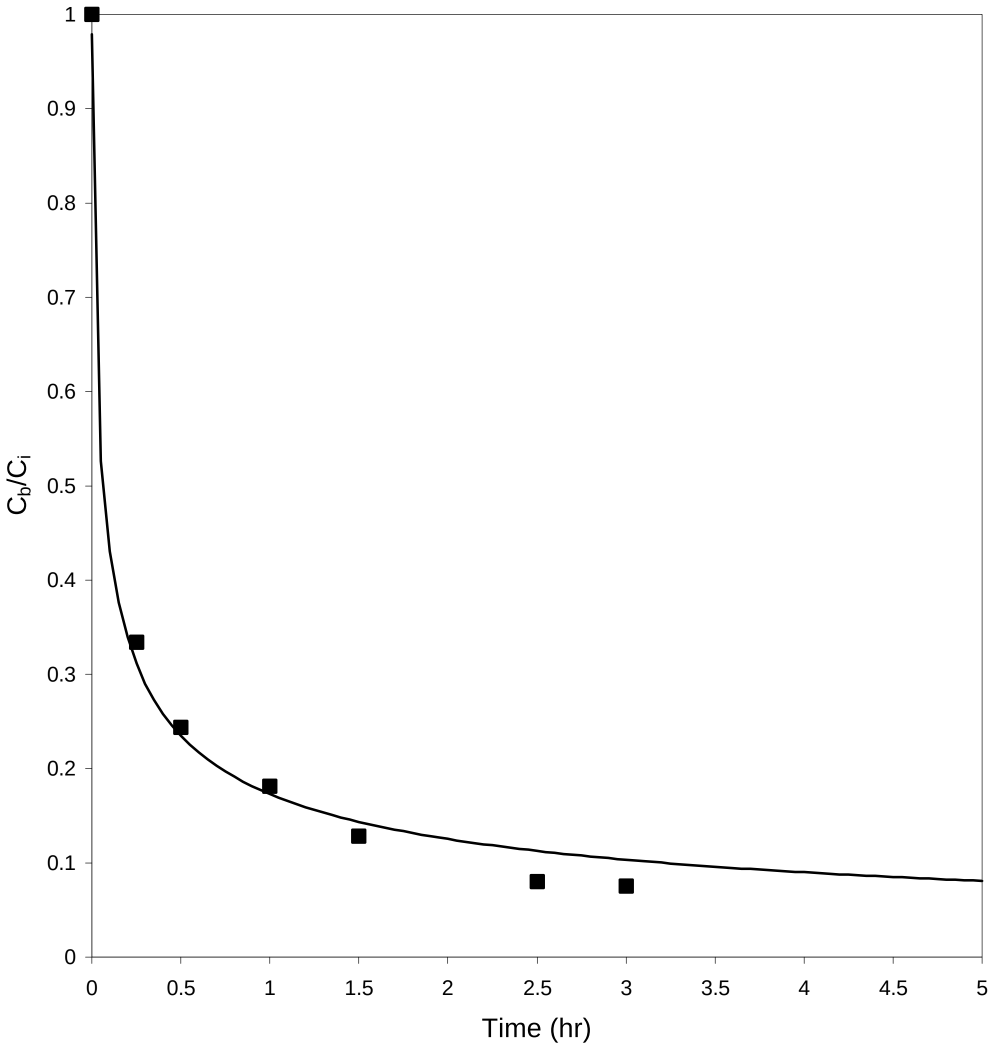

Figure 3. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of quinoline in cyclohexane on porous carbon catalyst (V=5ml, W=0.5g, T=27°C, K=2775cc/g)

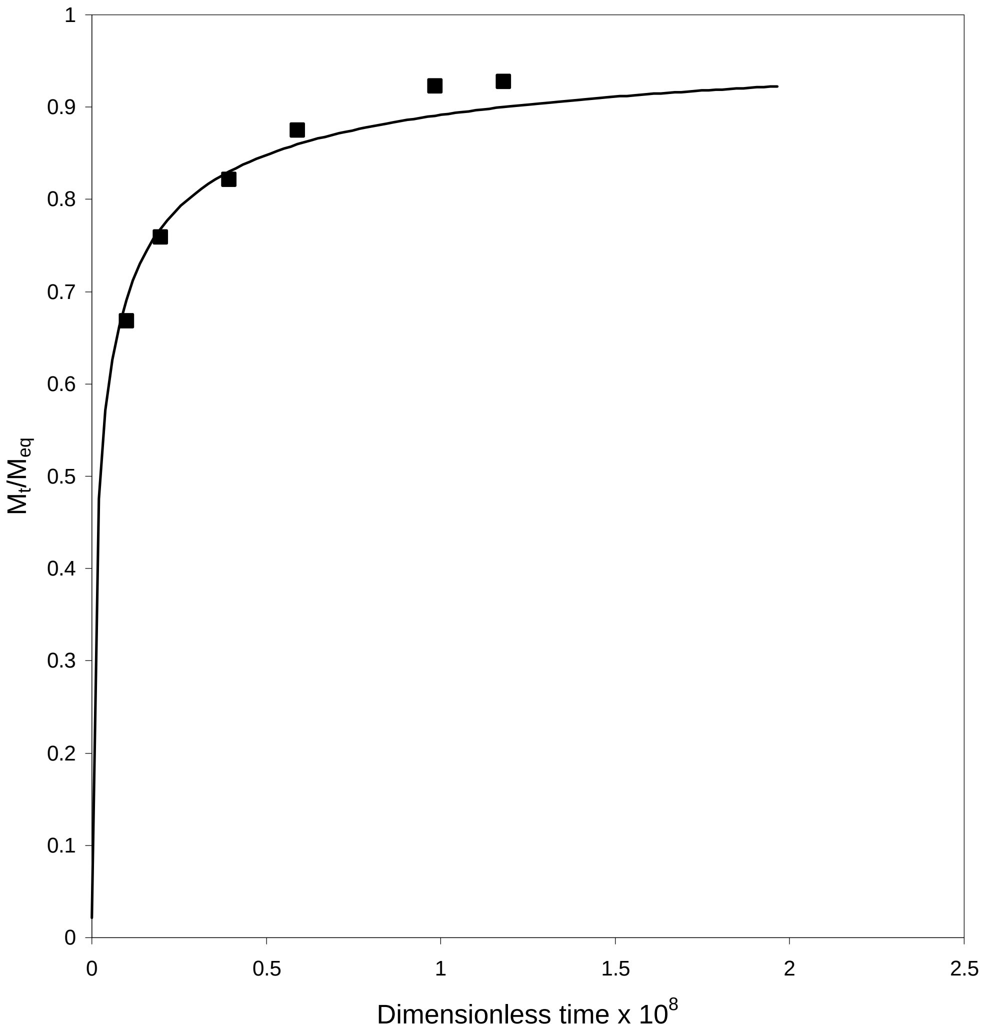

Figure 4. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of quinoline in cyclohexane on porous carbon catalyst (V=5ml, W=0.5g, T=27^{o}C, K=2775cc/g)

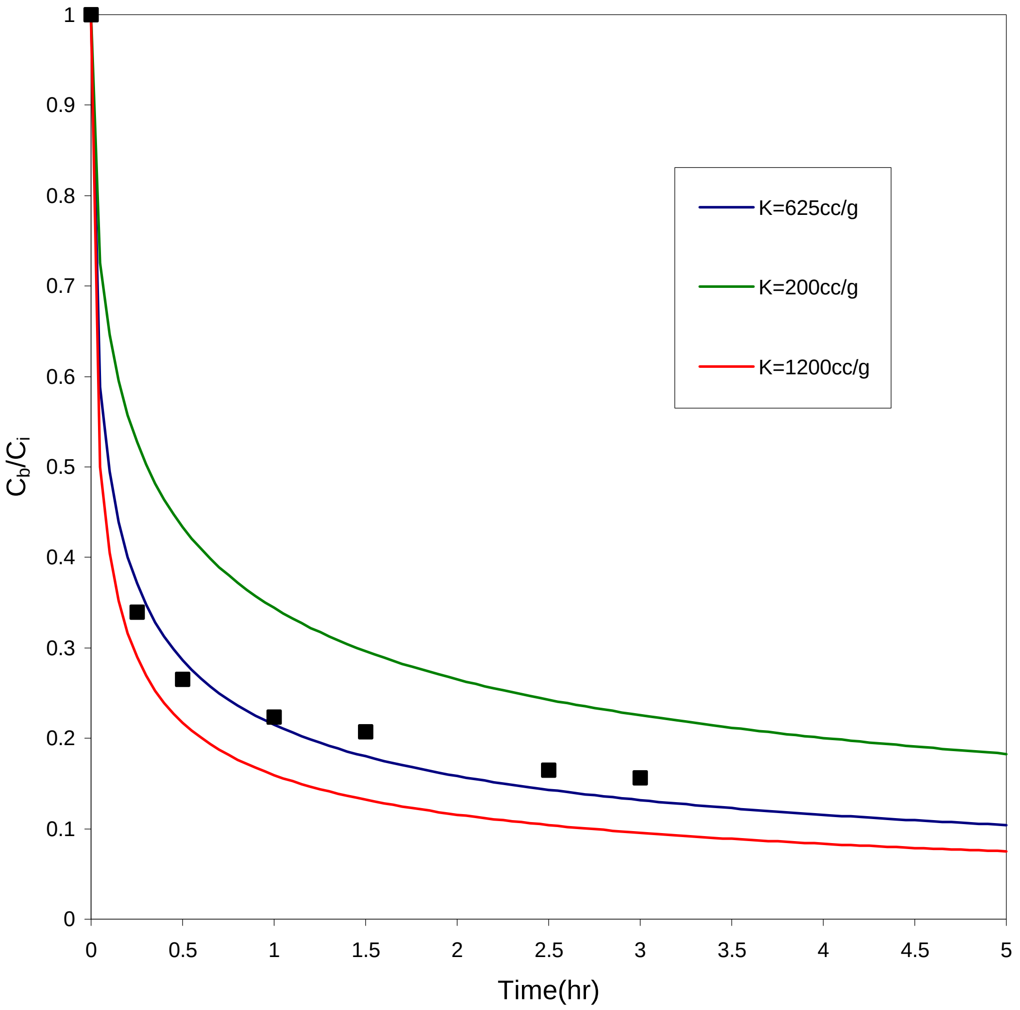

Figure 5. Comparison between experimental data and model simulation for the adsorptive uptake of quinoline in cyclohexane on porous carbon catalyst (V=10ml, W=1g, T=75°C)

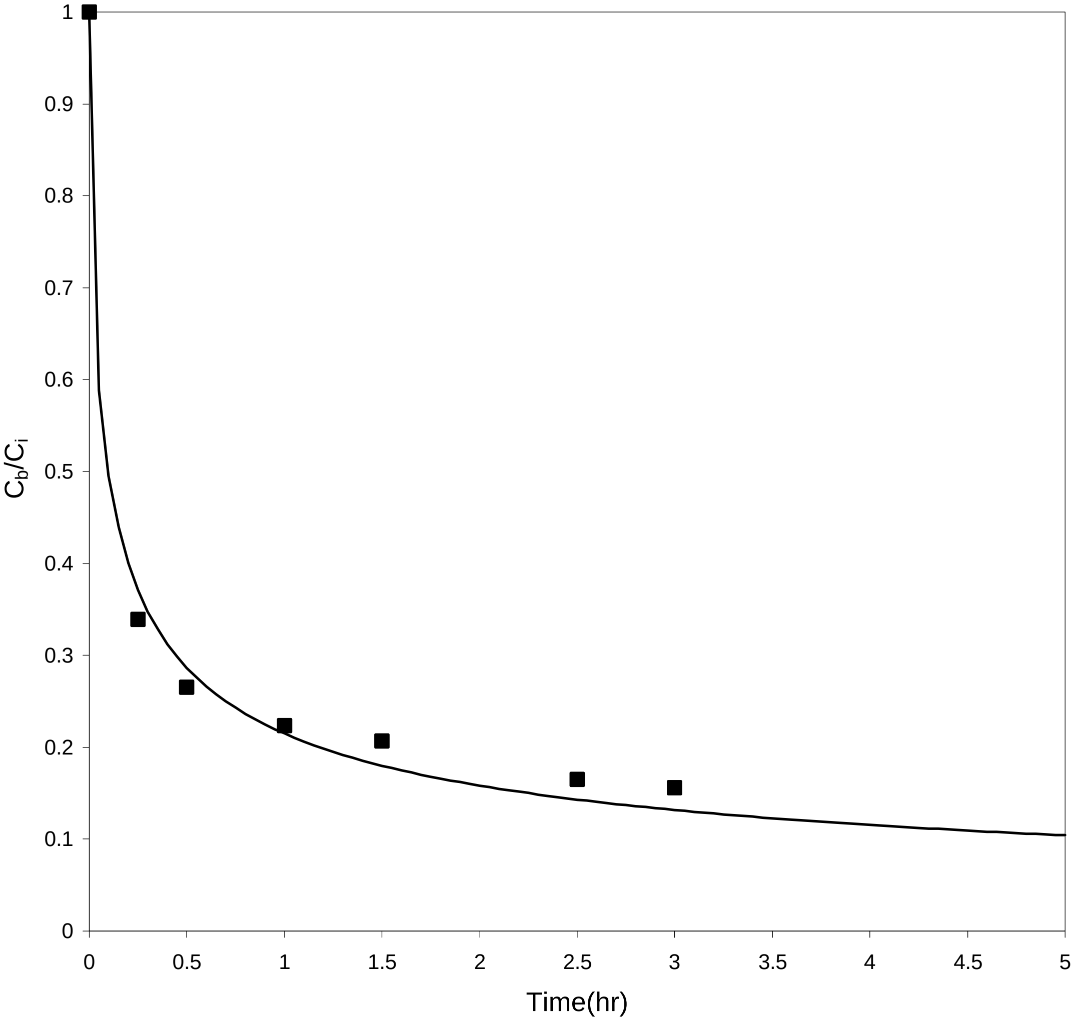

Figure 6. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of quinoline in cyclohexane on porous carbon catalyst (V=10ml, W=1g, T=75°C, K=625cc/g)

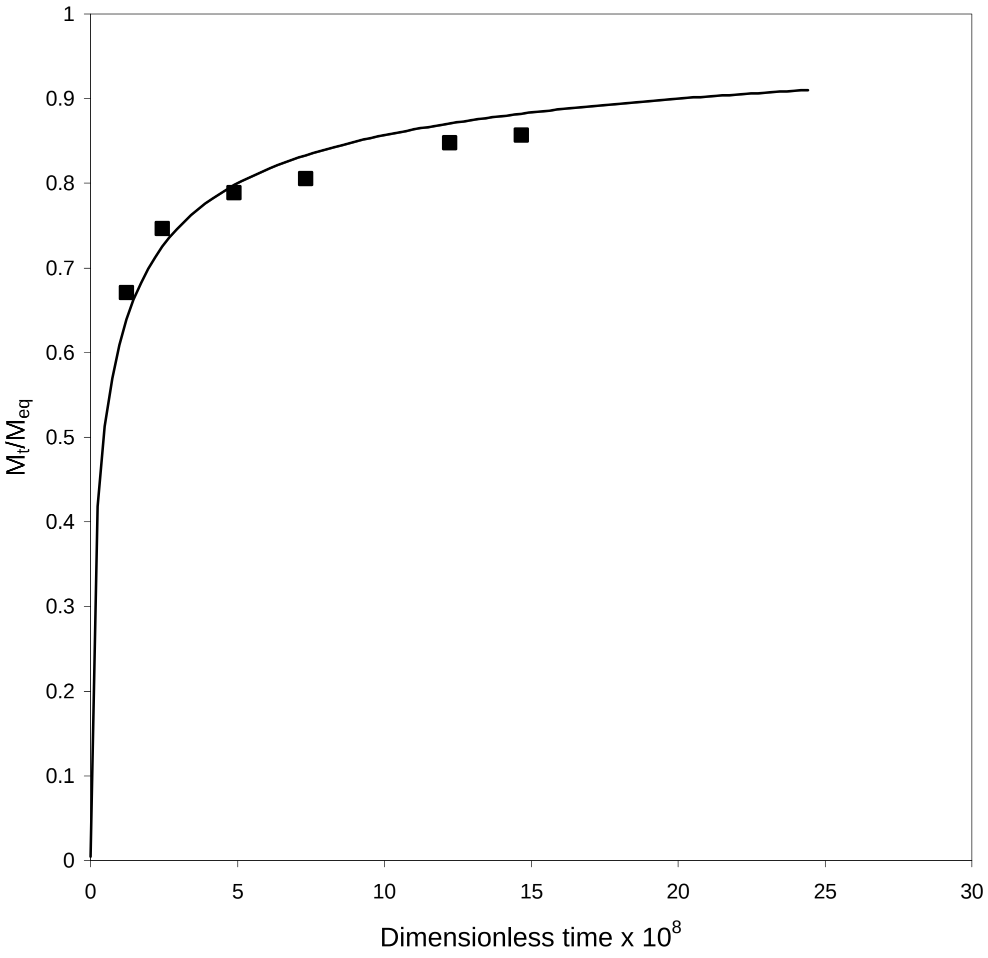

Figure 7. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of quinoline in cyclohexane on porous carbon catalyst (V=10ml, W=1g, T=75^{o}C, K=625cc/g)

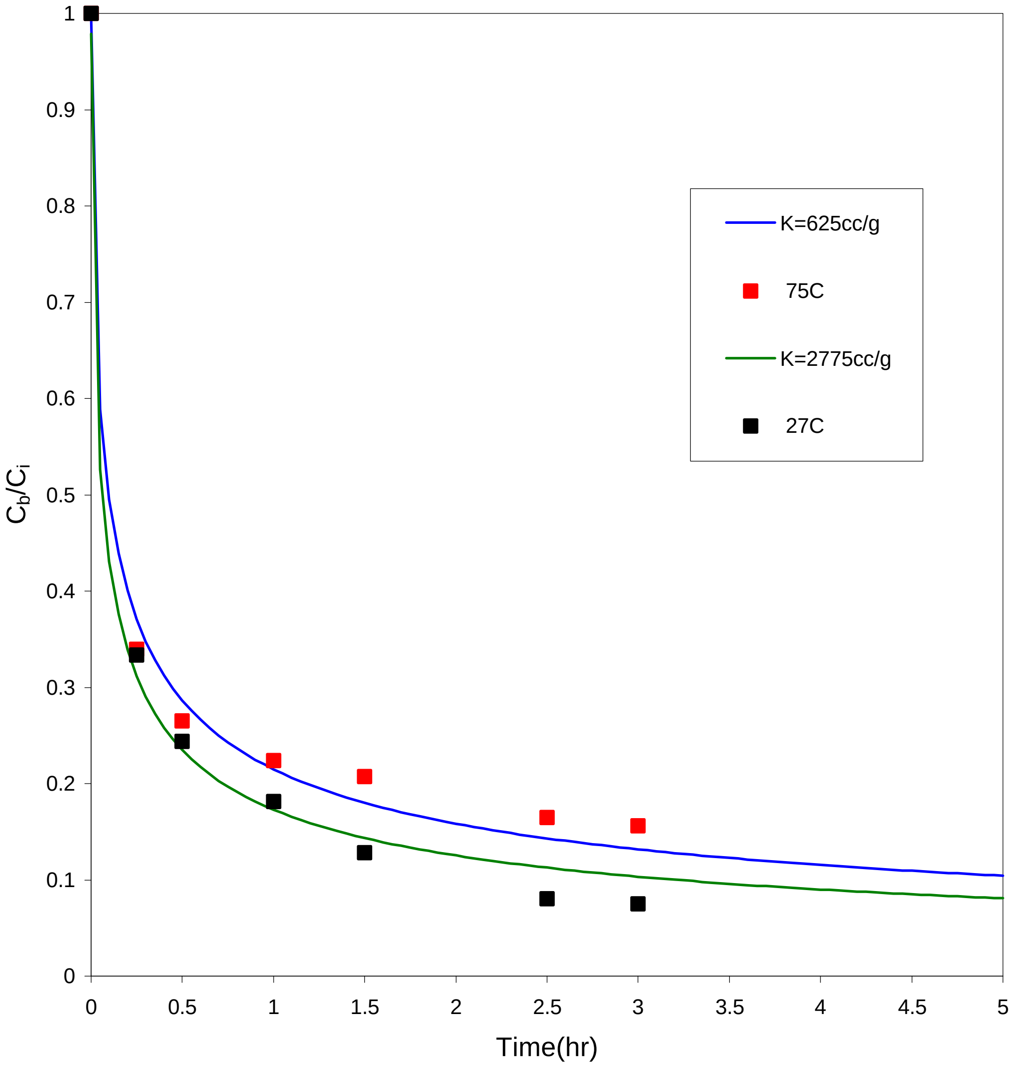

Figure 8. Effect of temperature on the adsorptive uptake of quinoline in cyclohexane on porous carbon catalyst (V/W=10cc/g)

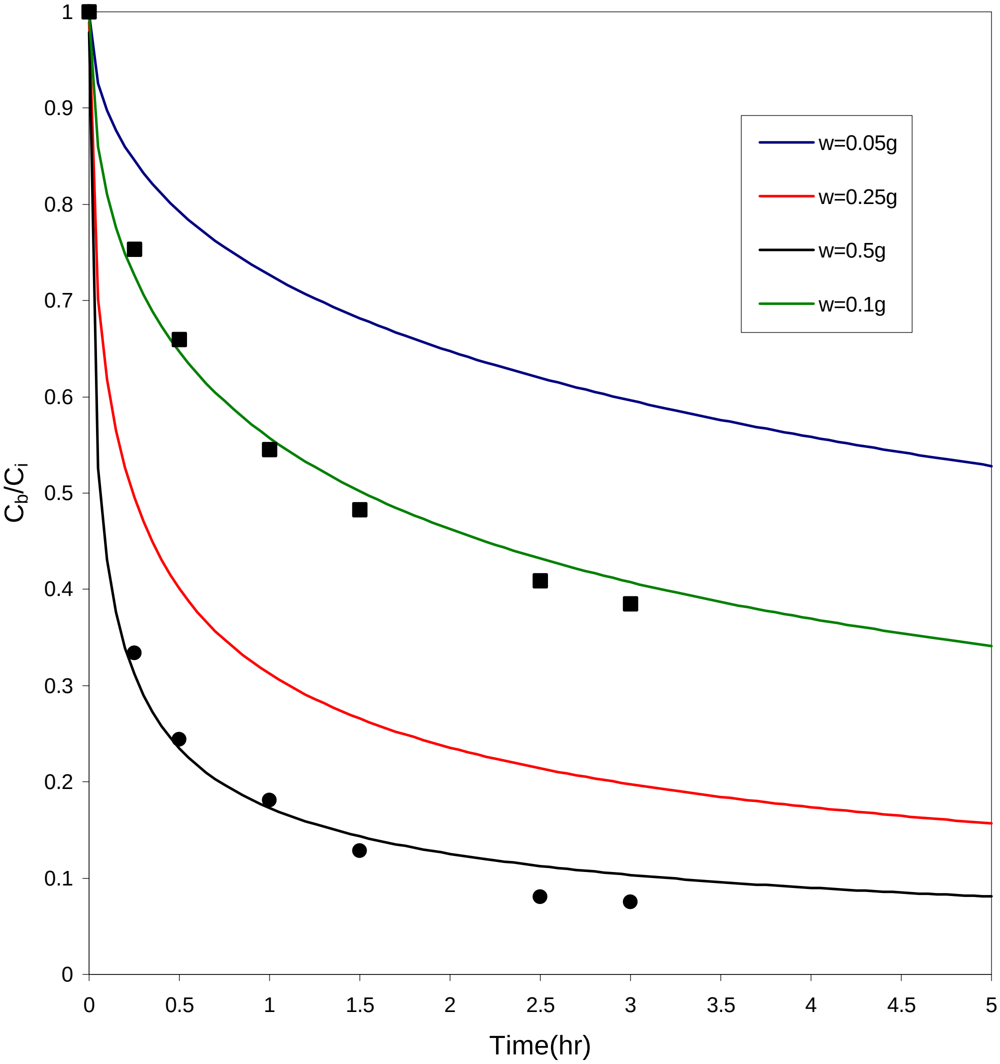

Figure 9. Comparison between experimental data and model simulation for the adsorptive uptake of quinoline in cyclohexane on porous carbon catalyst (V=5ml, T=27^{o}C, K=2775cc/g)

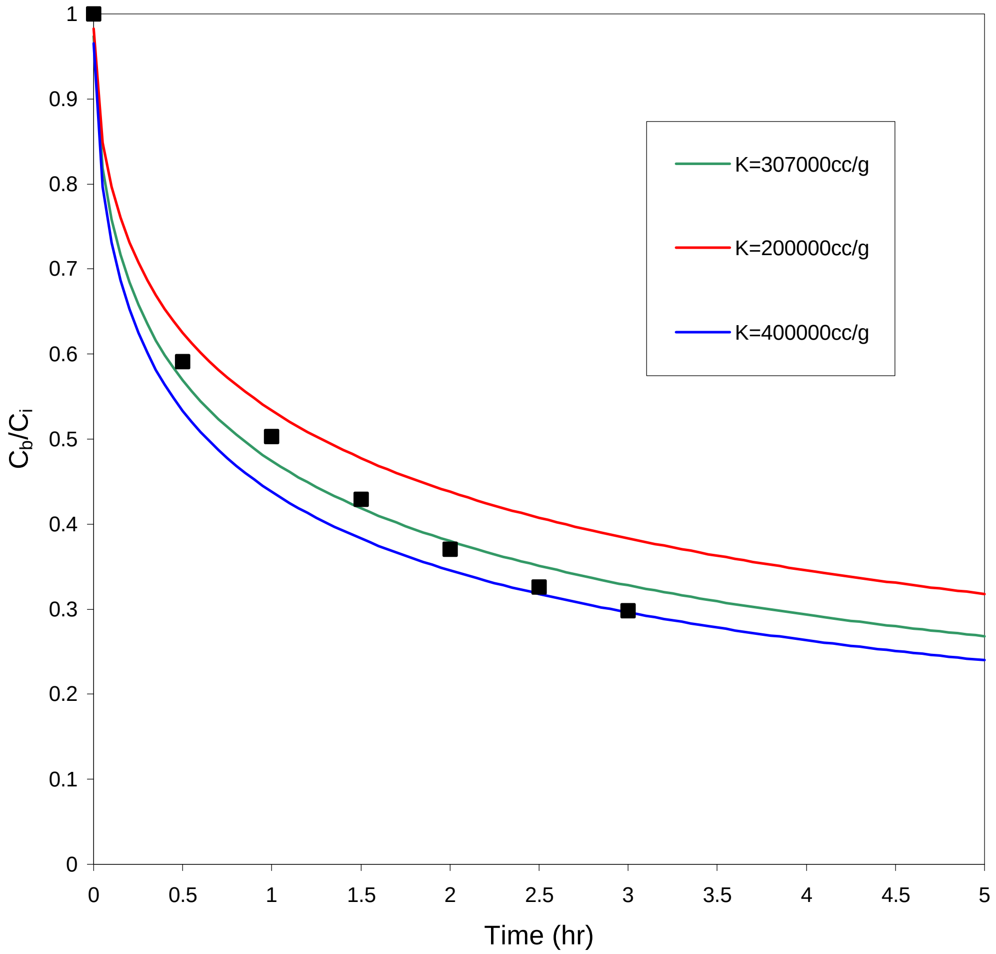

Figure 10. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in toluene on porous carbon catalyst (V=10ml, W=0.1g, T=27^{o}C)

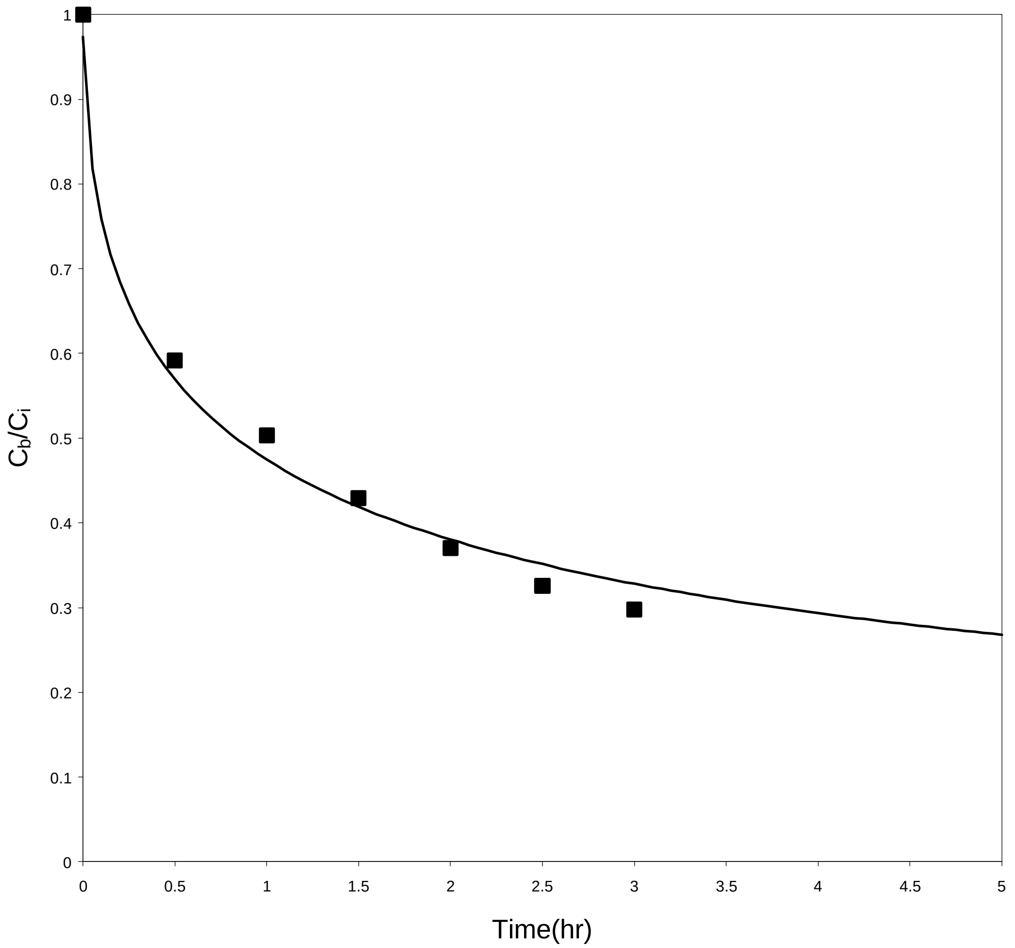

Figure 11. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in toluene on porous carbon catalyst (V=10ml, W=0.1g, T=27^{o}C, K=3.07 x 10^{5}cc/g)

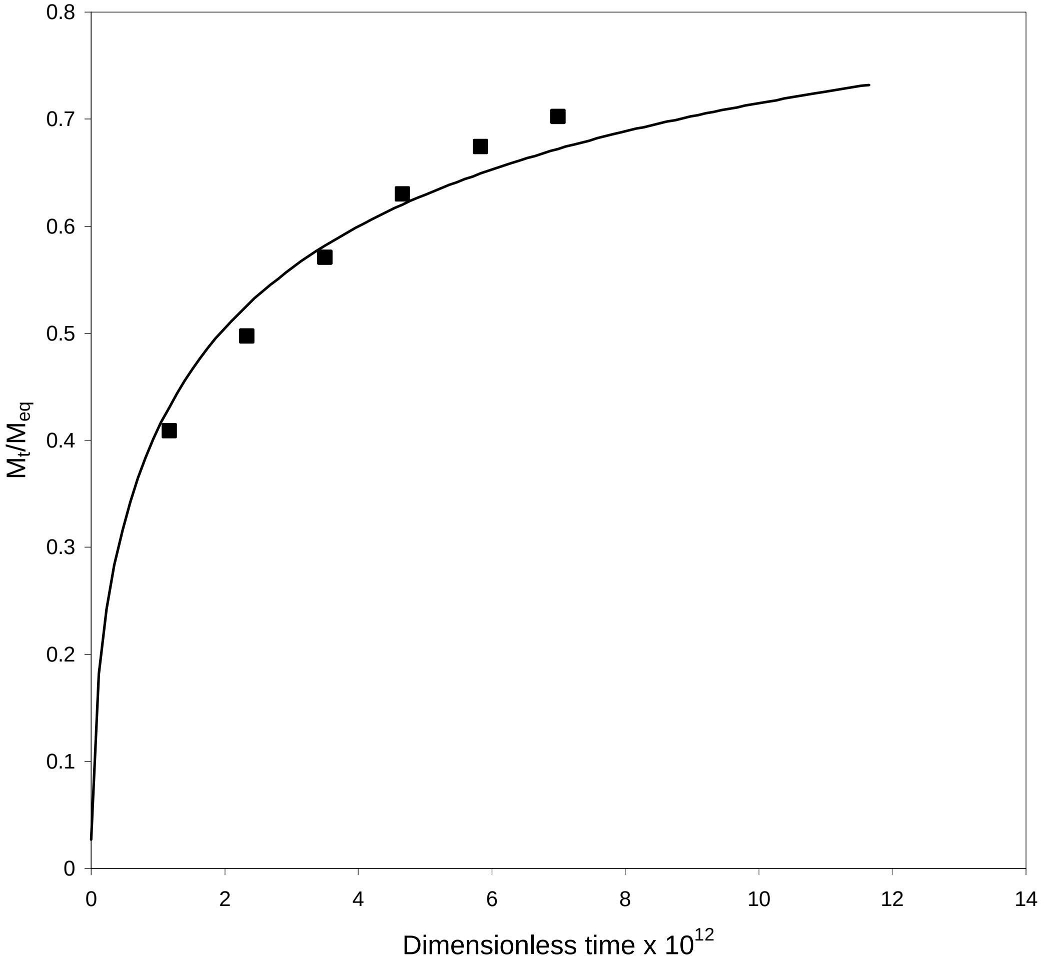

Figure 12. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in toluene on porous carbon catalyst (V=10ml, W=0.1g, T=27°C, K=3.07 x 10^5cc/g)

CONCLUSIONS

During this time period, experiments were performed in a microautoclave to study the diffusion controlled uptake of quinoline in cyclohexane,and a coal asphaltene, C-257K, in toluene onto a porous carbon substrate, rather than the alumina as used in the previous studies. A detailed comprehensive literature review was performed for the adsorptive uptake of various solutes on porous carbon substrates. A C++ program was written to simulate data using a mathematical model which incorporated diffusion and adsorption mechanisms. The simulation results showed that the mathematical model satisfactorily fitted the adsorptive diffusion of quinoline and C-257K onto activated carbon. In agreement with adsorption being an exothermic process, the adsorption constant for the quinoline/cyclohexane system decreased with increase in temperature from 27^{o}C to 75^{o}C. The adsorption constant for the C-257K/toluene system at 27^{o}C was much higher than that of the quinoline/cyclohexane system at the same temperature, indicating a possibly much greater affinity of the coal asphaltenes for the carbon surface.

NOMENCLATURE

Letters

C_b	solute bath concentration, g/cm^3
C_e	equilibrium solution phase concentration, g/cm^3
C_i	initial solute bath concentration, g/cm^3
C_r	concentration of solute in pore volume at a distance r where r is the distance in radial direction of the particle, g/cm^3
D_∞	solute molecular diffusivity, cm^2/s
D_e	solute effective diffusivity, cm^2/s
k	Boltzmann constant, 1.38×10^{-16} erg/K
K	linear adsorption constant, cc/g
K_p	steric factor
K_r	drag factor
M_{eq}	total amount of solute in the catalyst particle at equilibrium, g/cm^3
M_s	molecular weight of solute
M_t	total amount of solute in the catalyst particle after time t, g/cm^3
q	mass of solute adsorbed per unit mass of adsorbent
r_m	solute molecular size, cm
T	temperature, ^{o}C
V	bath volume, cc
W	catalyst weight, g

Greek

ε	catalyst porosity
η	solvent viscosity, g/cm-s
τ	tortuosity
λ	ratio of solute molecular size to pore size

REFERENCES

Anderson,J.L., and Quinn,J.A., Biophysical J., 14, 130 (1974) as cited in Yang (1997).

Carter,M.C., Weber Jr.,W.J., and Olmstead,K.P., J. AWWA, 73(8),81,1992.

Cornel,P.K., Summers,R.S., and Roberts,P.V., J.Colloid Interface Sci., 110(1),149,1986.

Cornel,P., Roberts,P.V., and Summers,R.S., J.Envir.Eng., ASCE, 111(6),891, 1985.

Deen,W.M., AIChE J., 33,1409,1987.

Deen,W.M., Bohrer,M.P. and Epstein,N.B., AIChE J., 27(6),952,1981.

Ferry,J.D., J.Gen.Physiol., 20,95,1936 as cited in Deen (1987).

Furusawa,T., and Smith,J.M., Ind.Eng.Chem.Fundam., 12(2),197,1973.

Furusawa,K., and Yamamoto,K., J.Colloid Interface Sci., 96(1),268,1983.

Garcia,M.A.F., Utrilla,J.R., Toleda,I.B. and Castilla,C.M., Langmuir, 14(7), 1880,1998.

Harding,A.W., Foley,N.J., Norman,P.R., Francis,D.C., and Thomas,K.M., Langmuir, 14(14),3858,1998.

Kilduff,J.E., Karanfil,T., and Weber Jr.,W.J., J. AWWA, 90(5),76,1998.

Knappe,D.R.U., Matsui,Y., Snoeyink,V.L., Roche,P., Prados,M.J., and Bourbigot,M.M., Environmental Science & Technology, 32(11),1694,1998.

Lee,M.C., Crittenden,J.C., and Snoeyink,V.L., J.Envir.Eng., ASCE, 109(3), 631, 1983.

Lee, L-K, AIChE J., 24, 531, 1978.

Leyva-Ramos,R., and Geankoplis,C.J., Chem.Eng.Sci., 40(5),799,1985.

Lyn,D.A., J.Envir.Eng., 122(11),1013,1996.

Ma, Y. H. and Y. Y. Lee, AIChE J., 22, 147, 1976.

Mathews,A.P., and Weber,W.J., Chem.Eng.Comm., 25,157,1984.

Morris,G., and Newcombe,G., J.Colloid and Interface Science, 159,413,1993.

Neretnieks,I., Chem.Eng.Sci., 31,1029,1976.

Newcombe,G., and Drikas,M., Water Research, 27(1),161,1993.

Ouki,S.K., and Neufeld,R.D., J.Chem.Tech.Biotechnol., 70,3,1997.

Pappenheimer,J.R., Renkin,E.M., and Borrero,L.M., Am.J.Physiol., 167,13,1951 as cited in Yang (1997).

Perry,R.H., and Chilton,C.H., Chemical Engineers' Handbook, Fifth edition, McGraw-Hill, 1973.

Ravikumar,V.S., Tsotsis,T.T., and Sahimi,M., Ind.Eng.Chem.Res., 36,3154, 1997.

Ruckenstein,E., Vaidyanathan,A.S., and Youngquist,G.R., Chem.Eng.Sci., 26,1305,1971.

Summers,R.S., and Roberts,P.V., J.Envir.Eng., 113(6),1333,1987.

Vadlamani,S.R., Masters' Thesis, Auburn University, 1999.

Weber,T., and Chakravorti,R.K., AIChE J., 20(2),228,1974.

Wilmanski,K., and Breemen,A.N., Water Research, 26,773,1990.

Yang,X., Ph.D. Dissertation, Auburn University, 1997.

PLANNED WORK

During the next time period, the adsorptive diffusion of coal and petroleum asphaltenes in porous carbons at various temperatures will continue to be studied. In light of the broad range of pore sizes for the porous carbon substrate, some consideration of a two domain model as discussed in this report may be warranted. The M.S. student now working on the project, Mr. Ganesh Ramakrishnan will perform these investigations as his thesis research requirements for the M.S. degree in chemical engineering.