

Hindered Diffusion of Asphaltenes at Evaluated Temperature and Pressure

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James A. Guin
Surya Vadlamani

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Auburn University
Chemical Engineering Department
230 Ross Hall
Auburn, AL 36849

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Abstract

During this past six months we continued our ongoing studies of the diffusion controlled uptake of coal and petroleum asphaltenes into a porous carbon catalyst. Toluene was used as the solvent for experiments at 20°C and 75°C while 1-methylnaphthalene was the solvent for the higher temperature experiments at 100°C, 150°C and 250°C. All runs were made at a pressure of 250 psi (inert He gas). Experiments were performed at 20°C and 75°C, for the petroleum asphaltene/toluene system. For the coal asphaltene/toluene system, experiments were performed at 75°C. Experiments were performed at 100°C, 150°C and 250°C for the coal asphaltene/1-methylnaphthalene system. A comparison between the experimental data and model simulated data showed that the mathematical model satisfactorily fitted the adsorptive diffusion of both the coal and petroleum asphaltenes onto a porous activated carbon. The adsorption constant decreases with an increase in temperature for both, the coal asphaltene/1-methylnaphthalene system as well as the petroleum asphaltene/toluene system. It was found that the adsorption constant for the coal asphaltene/toluene system at 75°C was much higher than that of the petroleum asphaltene/toluene system at the same temperature providing evidence of the greater affinity of the coal asphaltenes for the carbon surface. This could be due to the presence of more functional heteroatomic groups in the coal asphaltenes compared to their petroleum counterparts.

Also during this time period, a new carbon catalyst support was prepared in our laboratory which will be used in adsorption experiments during the next phase of work.

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OBJECTIVES

1. To investigate the hindered diffusion of coal and petroleum asphaltenes in porous catalysts.
2. To examine the effects of temperature on the intraparticle diffusivity of asphaltenes.

EXECUTIVE SUMMARY

The general aim of this project is to obtain a better understanding of the diffusion controlled uptake of model compounds and asphaltenes in porous catalysts at various temperatures. To aid in the achievement of this goal, we have examined the diffusion of both coal and petroleum asphaltenes in a porous carbon. Experiments were performed at 20°C and 75°C, for a petroleum asphaltene with toluene as solvent; at 75°C for a coal asphaltene with toluene as solvent; and at 100°C, 150°C and 250°C for the same coal asphaltene with 1-methylnaphthalene as solvent. Our previously developed C++ program was used to simulate data using a mathematical model. A comparison between the experimental data and model simulated data showed that the mathematical model satisfactorily fitted the diffusion controlled adsorption of the coal and petroleum asphaltenes onto porous carbon. The adsorption constant for the coal asphaltene/toluene system at 75°C was found to be much higher than that of the petroleum asphaltene/toluene system at the same temperature. This suggests that the coal asphaltenes have a much greater affinity than the petroleum asphaltenes for the surface of the porous carbon. In keeping with theories of exothermic adsorption, the adsorption constant decreases with an increase in temperature for both, the coal asphaltene/1-methylnaphthalene system as well as the petroleum asphaltene/toluene system.

Also during this time period, we have prepared a laboratory carbon-based catalyst support which will be utilized for adsorption-diffusion experiments in the near future.

INTRODUCTION

A better understanding of the diffusion of macromolecules in catalyst pores would be of significant benefit in catalyst development since diffusion greatly influences the overall rate of chemical reactions in heterogeneous catalysis. Previously, the diffusion controlled adsorptive uptake of quinoline in cyclohexane at 27°C and 75°C, and a coal asphaltene in toluene at 27°C, onto a porous carbon were studied. To extend these studies, our objective during the current time period was to study the hindered diffusion of coal and petroleum asphaltenes in porous carbon at elevated temperatures and pressures. Therefore, we performed experiments to study the diffusion controlled adsorptive uptake of the coal asphaltene in toluene at 75°C; the coal asphaltene in 1-methylnaphthalene at 100°C, 150°C and 250°C; and a petroleum asphaltene in toluene at 20°C and 75°C, onto a porous carbon at 250 psi inert gas pressure. The effect of temperature on the adsorptive uptake was investigated for both the petroleum asphaltene/toluene system as well as the coal asphaltene/1-methylnaphthalene system during the time period covered by this report.

LITERATURE REVIEW

We would like to briefly revisit a small portion of the literature review covered in our previous report since it is essential for an understanding of this report as well. In this light, we recall that Anderson and Quinn (1974) made a comprehensive theoretical analysis of hindered diffusion while Deen (1987) reviewed many applications of theories of hindered transport through membranes. In these investigations, a widely used relation is the molecular diffusivity as given by the Stokes Einstein equation

$$D_{\infty} = kT/6\pi\eta r_m \quad (1)$$

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,

$$D_e = K_p K_r \epsilon D_{\infty} / \tau \quad (2)$$

where K_p is the steric factor, K_r is the drag factor, ϵ is the porosity and τ is the tortuosity.

Ferry (1936) studied the steric factor and postulated that

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

where λ is the ratio of molecular size to pore size. The drag factor can be estimated using the relation given by Pappenheimer et al. (1951)

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

In our mathematical simulation of the diffusion process, we use equations (3) and (4) to provide estimates of the effective diffusivity of asphaltenes in catalyst pores.

EXPERIMENTAL SECTION

Materials

In the case of the coal asphaltene/toluene system, the asphaltene used was termed C-257K (obtained from the Wilsonville Advanced Coal Liquefaction Research and Development Facility, Wilsonville, Alabama) while toluene (Fisher Scientific) was the solvent. C-257K also was used along with 1-methylnaphthalene (Aldrich Chemical Company) for the coal asphaltene/1-methylnaphthalene system. For the petroleum asphaltene/toluene system, the asphaltene utilized was termed P-AAD (obtained from a California Valley petroleum asphalt source). The properties of the coal and petroleum asphaltenes, C-257K and P-AAD respectively are given in the dissertation by Yang (1997), a previous PhD candidate on the project. The same porous carbon catalyst, with an irregular shape, an equivalent particle radius of 0.2cm and a surface area of 1100 m²/g was used as the adsorption-diffusion medium for all 3 systems. Additional properties of the porous carbon catalyst are given in Table 1. The pore size distribution for the catalyst is given in Figure 1.

Apparatus and Procedures for Each Solute/Solvent System.

1. Coal asphaltene/toluene system

A microautoclave batch reactor was used to study the adsorptive uptake of coal asphaltene, C-257K in toluene on porous activated carbon at 75°C. The porous carbon particles, presoaked in toluene, were supported in a wire mesh compartment in the microautoclave to avoid direct contact with the solution until the experiment was begun.

Air was removed from the system by purging the microautoclave with helium 5 times. Then, the microautoclave was left pressurized to 250 psig with helium for the duration of the experiment. The microautoclave was attached to a horizontal agitator and lowered into a fluidized sand bath whose temperature was maintained by a temperature controller. The runs were made for various time periods with an initial C-257K concentration corresponding to 0.05 g/L. On completion of a run, the liquid phase was collected and filtered. The C-257K concentration in the liquid phase after the diffusional uptake experiments was obtained by analysis using a UV-VIS spectrophotometer at 400nm.

2. Petroleum asphaltene/toluene system

In these experiments, the basic procedure remained the same as above except for the fact that the solute was now the petroleum asphaltene, P-AAD. The initial concentration of asphaltene P-AAD was 0.07g/L of solution. The experiments were performed at 20°C and 75°C. The P-AAD concentration in the liquid phase after the diffusional uptake experiments was obtained also by analysis using a UV-VIS spectrophotometer at 400nm.

3. Coal asphaltene/1-methynaphthalene system

Once again, the basic procedure remained the same as above except for the fact that the solute was now C-257K and the solvent was 1-methynaphthalene. The initial concentration of asphaltene C-257K was 0.02 g/L of solution. The experiments were performed at 100°C, 150°C and 250°C. The C-257K concentration following the diffusional uptake experiments was obtained as before.

RESULTS AND DISCUSSION

I Coal asphaltene / toluene system

1. Effective and molecular diffusivities

From our earlier work (Yang, 1997), the molecular weight of coal asphaltene C-257K was estimated to be 490. Further, Yang (1997), obtained a relation for the size of the asphaltene as a function of the molecular weight as:

$$r_m = 0.36 M_s^{0.5} \quad (5)$$

where M_s is the molecular weight of the asphaltene. The radius of the C-257K molecule was determined to be 7.97×10^{-8} cm using equation (5). At the experimental temperature of 75°C , the viscosity of toluene is 0.34 cP (Perry and Chilton, 1973). Using these values and the average pore radius in Table 1 in equation (1), we estimate the value of molecular diffusivity D_∞ to be 9.402×10^{-6} cm²/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. Using these values in equation (2), we find the value of effective diffusivity D_e to be 4.294×10^{-8} cm²/s. The above values of estimated parameters are given in Table 2.

2. Comparison of experimental data with model simulations

The experimental adsorptive uptake data for the coal asphaltene C-257K/toluene system at 75°C is given in Table 8. This data is compared with the uptake process as simulated by the mathematical model as developed in our previous project reports. The value of K which best fits the experimental data was found to be 9×10^4 cc/g by least square analysis. Figure 2 shows the comparison between the experimental data and model

simulations for three different values of K (4×10^4 , 9×10^4 and 1.5×10^5 cc/g). The comparison between the experimental data and model simulation for the best fit value of K are shown by Figures 3 and 4.

3. Adsorption Constant

For the coal asphaltene C-257K/toluene system at 75°C, the value of the adsorption constant was determined to be 9×10^4 cc/g. In our previous work, the value of the adsorption constant for the coal asphaltene C-257K/toluene system at 27°C was found to be 3.07×10^5 cc/g. Hence, in keeping with general theories of exothermic adsorption, the adsorption constant for the C-257K/toluene system decreases with the increase in temperature.

II Petroleum asphaltene P-AAD / toluene system

1. Effective and molecular diffusivities

a) Experiments at 20°C

In our earlier work (Yang, 1997), the molecular weight of petroleum asphaltene P-AAD was estimated to be 2200. The radius of the P-AAD molecule is determined to be 16.89×10^{-8} cm using equation (5). In this case, the solute molecule size is greater than the average pore radius previously used for the carbon catalyst. This fact arises because the carbon catalyst contains some pores which are actually smaller than the asphaltenes, and hence are not accessible for adsorption. Therefore a new approach is developed to determine a new average pore size, taking into account only the accessible pores. In this new method, the assumptions are

- 1) We will not consider the pores which are smaller than 16.89×10^{-8} cm (the size of the asphaltene molecules).
- 2) For the remaining pores, we will find an average pore radius which we shall term the effective (i. e., accessible), average pore radius.

Using these procedures, the effective (accessible) porosity, effective pore volume and effective surface area of the porous carbon were determined to be 0.27, 0.35 cc/g and 85.712×10^4 cm²/g, respectively. Based on these values, the effective average pore radius was found to be 81.67×10^{-8} cm. At the experimental temperature of 20°C, the viscosity of toluene is 0.58 cP (Perry and Chilton, 1973). Using equation (1), we obtain the value of molecular diffusivity D_{∞} to be 2.19×10^{-6} cm²/s. Using equation (3), we find that the steric factor K_p is 0.6292 and from equation (4), we find that the hydrodynamic factor K_r is 0.583. Using these values in equation (2), we find the value of effective diffusivity D_e to be 5.42×10^{-8} cm²/s. The above values of estimated parameters are summarized in Table 3.

b) Experiments at 75°C

By accounting for the effect of temperature on viscosity, and then using equation (1), the value of D_{∞} at 75°C was found to be 4.437×10^{-6} cm²/s. From equation (2), we find the corresponding value of D_e to be 1.099×10^{-7} cm²/s. Table 4 records these values.

2. Comparison of experimental data with model simulations

The experimental adsorptive uptake data for the petroleum asphaltene P-AAD/toluene system at 20°C and 75°C are given in Tables 9 and 10, respectively. This data is

compared with the uptake simulated by the mathematical model for the diffusion-controlled uptake process as developed in our previous project reports. The value of K which best fits the experimental data at 20°C was found to be 2.4×10^3 cc/g by least square analysis. Figure 5 shows the comparison between the experimental data and model simulations for three different values of K (1.4×10^3 , 2.4×10^3 and 3.4×10^3 cc/g) at 20°C. The comparison between the experimental data and model simulation for the best fit value of K at 20°C are shown by Figures 6 and 7. The value of K which best fits the experimental data at 75°C was found to be 1010 cc/g by least square analysis. Figure 8 shows the comparison between the experimental data and model simulations for three different values of K (500, 1010 and 1800 cc/g) at 75°C. The comparison between the experimental data and model simulation for the best fit value of K at 75°C are shown by Figures 9 and 10. In general, the comparisons between model simulations and experimental data are fairly satisfactory; although, the data do tend to lie above the model curve at early times and decline below the curve a later times. The exact reasons for this are not completely clear, but could involve multilayer adsorption, or the more complex pore structure of the porous carbons.

3. Adsorption Constant

For the petroleum asphaltene P-AAD/toluene system, the value of the adsorption constant is 2400 cc/g at 20°C. At 75°C, the value of the adsorption constant is 1010 cc/g. Table 14 records these values. In line with the previously observed behavior, the adsorption constant for the P-AAD/toluene system also decreases with increasing temperature.

Hence, as shown in Figure 11, the net adsorptive uptake decreases with increasing temperature.

III Coal asphaltene / 1-methylnaphthalene system

1. Effective and molecular diffusivities

a) Experiments at 100°C

As we have seen earlier, the radius of the C-257K molecule was determined to be 7.97×10^{-8} cm. At the experimental temperature of 100°C, the viscosity of 1-methylnaphthalene is 0.9 cP (Yaws, 1995). Using these values and the average pore radius in Table 1 in equation (1), we obtain the value of molecular diffusivity D_{∞} to be 3.81×10^{-6} cm²/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. Using these values in equation (2), we find the value of effective diffusivity D_e to be 1.74×10^{-8} cm²/s. The above values of estimated parameters are recorded in Table 5.

b) Experiments at 150°C

Accounting for the effect of temperature on viscosity, and then using equation (1), the value of D_{∞} obtained is 7.06×10^{-6} cm²/s. From equation (2), we find the corresponding value of D_e to be 3.22×10^{-8} cm²/s. The above values of estimated parameters are recorded in Table 6.

c) Experiments at 250°C

In a similar manner, the D_{∞} obtained is $1.601 \times 10^{-5} \text{ cm}^2/\text{s}$ and the corresponding value of D_e is $7.31 \times 10^{-8} \text{ cm}^2/\text{s}$. as recorded in Table 7.

2. Comparison of experimental data with model simulations

The experimental adsorptive uptake data for the C-257K/1-methylnaphthalene system at 100°C, 150°C and 250°C are given in Tables 11, 12 and 13, respectively. This data is compared with the uptake simulated by the mathematical model for the diffusion-controlled uptake process as developed in our previous project reports. The value of K which best fits the experimental data at 100°C was found to be $6.2 \times 10^4 \text{ cc/g}$ by least square analysis. Figure 12 shows the comparison between the experimental data and model simulations for three different values of K (10^4 , 6.2×10^4 and $1.2 \times 10^5 \text{ cc/g}$) at 100°C. The comparison between the experimental data and model simulation for the best fit value of K at 100°C are shown by Figures 13 and 14. The value of K which best fits the experimental data at 150°C was found to be 12,775 cc/g by least square analysis. Figure 15 shows the comparison between the experimental data and model simulations for three different values of K (2×10^3 , 12,775 and $3 \times 10^4 \text{ cc/g}$) at 150°C. The comparison between the experimental data and model simulation for the best fit value of K at 150°C is shown by Figures 16 and 17. The value of K which best fits the experimental data at 250°C was found to be 1050 cc/g by least square analysis. Figure 18 shows the comparison between the experimental data and model simulations for three different values of K (100, 1050 and 10^4 cc/g) at 250°C. The comparison between the

experimental data and model simulation for the best fit value of K at 250°C is shown by Figures 19 and 20.

3. Adsorption Constant

For the C-257K/1-methylnaphthalene system, at 100°C, 150°C and 250°C, the best values of the adsorption constant were determined to be 6.2×10^4 , 12,775 and 1050 cc/g, respectively. Table 14 records these values. From these values, it is clear that the adsorption constant for the C-257K / 1-methylnaphthalene system decreases with increases in temperature. Hence, as shown in Figure 21, the net adsorptive uptake decreases with increases in temperature.

IV Preparation of Carbon Catalyst

Carbon supported catalysts are of interest in many areas, including hydrotreating, based on their tendency to form less coke, and hence undergo less catalyst deactivation than the corresponding metal oxide supports. The diffusion of asphaltenes and other species in these porous carbon supports would be of interest in this regard. Thus, several carbon catalyst supports were prepared in the laboratory during this quarter based on carbonization of a mixture of binder and carbon black (Schmitt, Jr., 1976, Vissers, 1987). To prepare the catalysts, a mixture of carbon black spheres is mixed with an appropriate amount of a resorcinol resin two-part binder. The resulting mixture is extruded through a dye and then allowed to dry for a certain time period. Following drying, the extrudates are carbonized in a tube furnace at 600° C for 2 hours under an inert flowing nitrogen atmosphere. This process converts the binder to carbon. The resulting extrudates had

good strength and are in the process of being characterized for pore size distribution. It is expected that the pore size can be varied by preparing the extrudates with different size carbon black particles. The diffusional properties of these laboratory prepared supports will be investigated in the next time period.

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 C-257K / toluene system at 75°C

Viscosity ^(a)	0.34 cP
Molecular diffusivity ^(b)	$9.402 \times 10^{-6} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$4.294 \times 10^{-8} \text{ cm}^2/\text{s}$

(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 P-AAD / toluene system at 20°C

Viscosity ^(a)	0.58 cP
Molecular diffusivity ^(b)	$2.19 \times 10^{-6} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$5.42 \times 10^{-8} \text{ cm}^2/\text{s}$

(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 P-AAD / toluene system at 75°C

Viscosity ^(a)	0.34 cP
Molecular diffusivity ^(b)	$4.437 \times 10^{-6} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$1.099 \times 10^{-7} \text{ cm}^2/\text{s}$

(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. Parameter values for the C-257K / 1-methylnaphthalene system at 100°C

Viscosity ^(a)	0.9 cP
Molecular diffusivity ^(b)	$3.81 \times 10^{-6} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$1.74 \times 10^{-8} \text{ cm}^2/\text{s}$

(a) Obtained from Yaws (1995)

(b) Calculated from equation (1)

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

Table 6. Parameter values for the C-257K / 1-methylnaphthalene system at 150°C

Viscosity ^(a)	0.55 cP
Molecular diffusivity ^(b)	$7.06 \times 10^{-6} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$3.22 \times 10^{-8} \text{ cm}^2/\text{s}$

(a) Obtained from Yaws (1995)

(b) Calculated from equation (1)

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

Table 7. Parameter values for the C-257K / 1-methylnaphthalene system at 250°C

Viscosity ^(a)	0.3 cP
Molecular diffusivity ^(b)	$1.601 \times 10^{-5} \text{ cm}^2/\text{s}$
Effective diffusivity ^(c)	$7.31 \times 10^{-8} \text{ cm}^2/\text{s}$

(a) Obtained from Yaws (1995)

(b) Calculated from equation (1)

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

Table 8. Experimental data for the C-257K / toluene system at 75°C
(V=10ml, W=0.1g)

Time, hr	C_b/C_I	M_t/M_{eq}
0	1	0
0.5	0.614	0.387
1	0.546	0.455
1.5	0.5	0.5
2	0.468	0.533
2.5	0.445	0.555
3	0.429	0.571

Table 9. Experimental data for the P-AAD / toluene system at 20°C
(V=10ml, W=0.1g)

Time, hr	C_b/C_I	M_t/M_{eq}
0	1	0
2	0.885	0.12
6	0.768	0.241
8	0.731	0.28
16	0.621	0.395
24	0.555	0.463

Table 10. Experimental data for the P-AAD / toluene system at 75°C
(V=10ml, W=0.1g)

Time, hr	C_b/C_I	M_t/M_{eq}
0	1	0
2	0.891	0.12
6	0.791	0.23
8	0.751	0.274
16	0.64	0.396
24	0.58	0.462

Table 11. Experimental data for the C-257K / 1-methylnaphthalene system at 100°C (V=10ml, W=0.1g)

Time, hr	C_b/C_I	M_t/M_{eq}
0	1	0
2	0.653	0.348
4	0.559	0.441
8	0.453	0.547
12	0.381	0.62
16	0.339	0.662
24	0.284	0.717

Table 12. Experimental data for the C-257K / 1-methylnaphthalene system at 150°C (V=10ml, W=0.1g)

Time, hr	C_b/C_I	M_t/M_{eq}
0	1	0
2	0.712	0.29
4	0.682	0.32
8	0.614	0.389
12	0.551	0.453
16	0.462	0.542
24	0.394	0.611

Table 13. Experimental data for the C-257K / 1-methylnaphthalene system at 250°C (V=10ml, W=0.1g)

Time, hr	C_b/C_I	M_t/M_{eq}
0	1	0
2	0.911	0.097
4	0.852	0.162
8	0.763	0.26
12	0.712	0.315
16	0.691	0.338
24	0.661	0.371

Table 14. Adsorption constant values

System	Temperature (°C)	Adsorption Constant (cc/g)
C-257K/toluene	75	9×10^4
P-AAD/toluene	20	2400
P-AAD/toluene	75	1010
C-257K/1-methylnaphthalene	100	6.2×10^4
C-257K/1-methylnaphthalene	150	12,775
C-257K/1-methylnaphthalene	250	1050

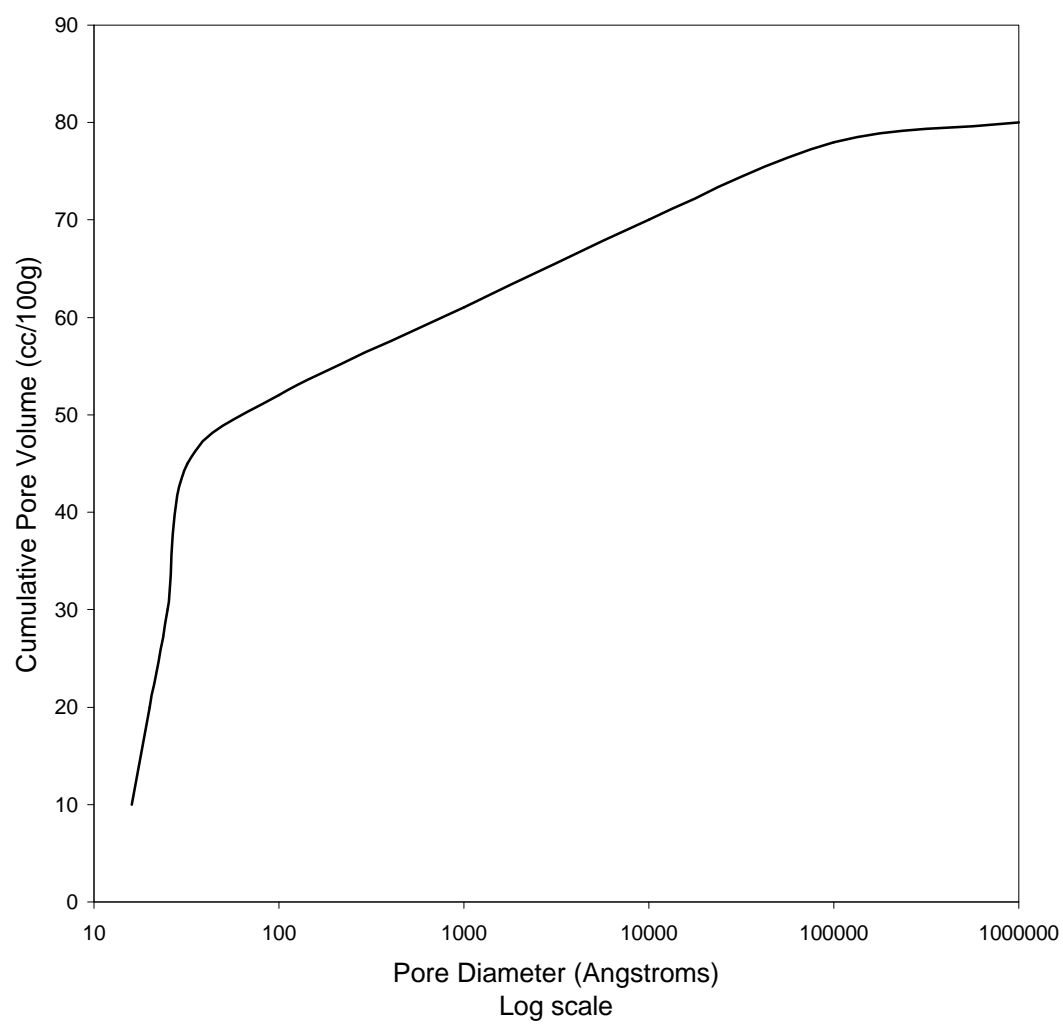


Figure 1. Pore Size Distribution of Calgon Carbon's BPL 4 x 6 porous carbon (from Product Bulletin of Calgon Carbon, 1997)

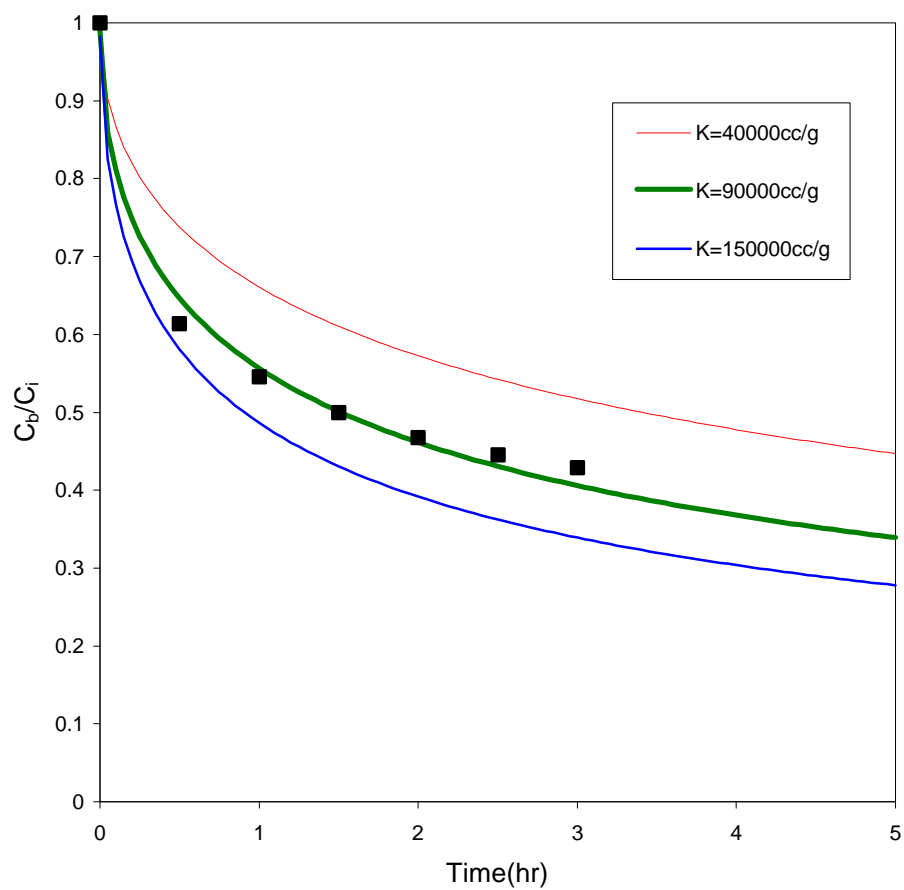


Figure 2. Comparison between experimental data and model simulation for the adsorptive uptake of C-257K in toluene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=75^\circ\text{C}$)

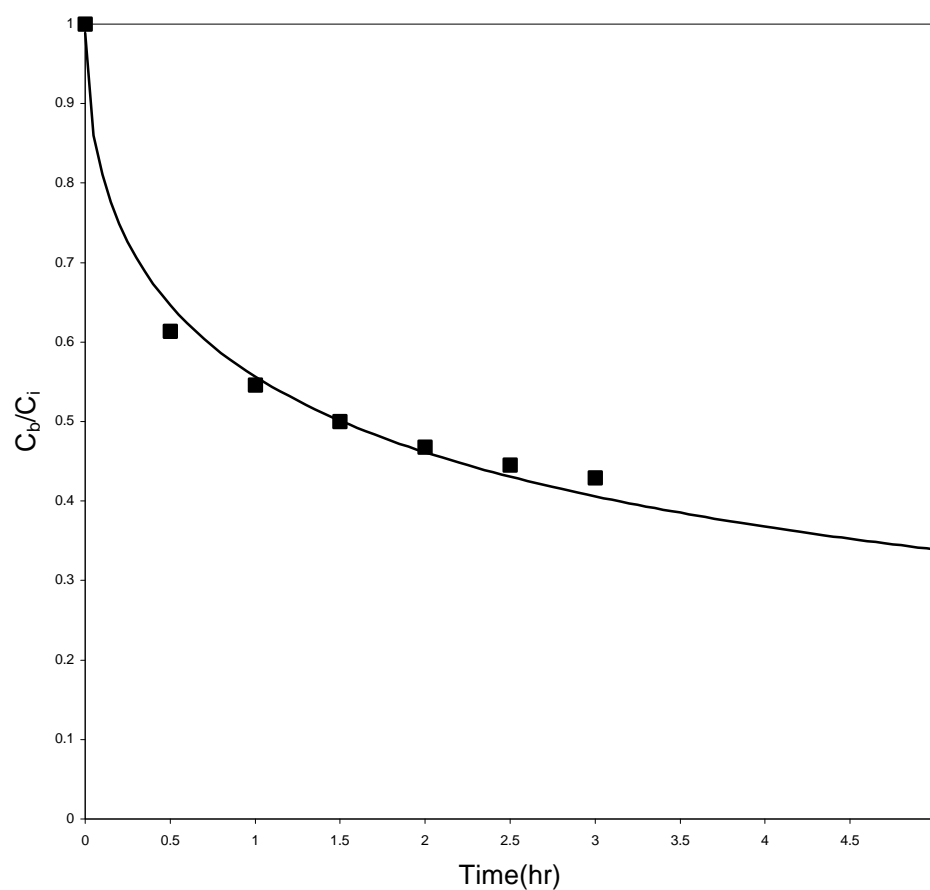


Figure 3. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in toluene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=75^\circ\text{C}$, $K=9 \times 10^4\text{cc/g}$)

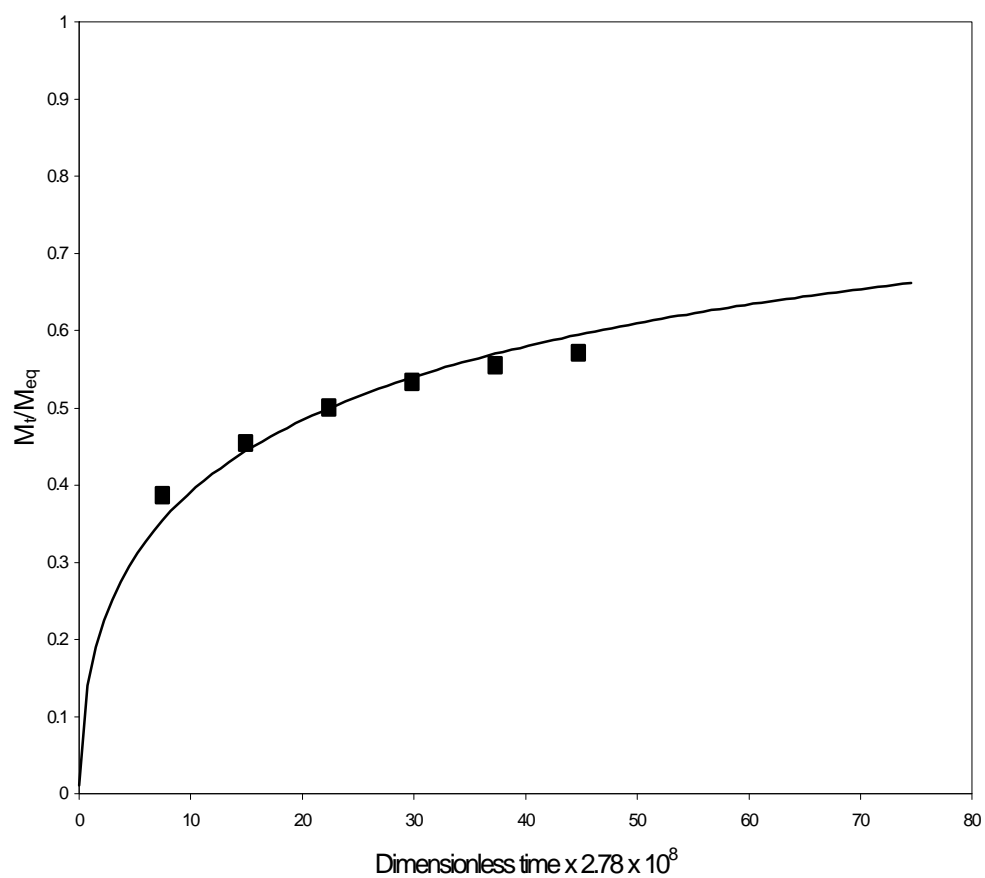


Figure 4. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in toluene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=75^\circ\text{C}$, $K=9 \times 10^4 \text{cc/g}$)

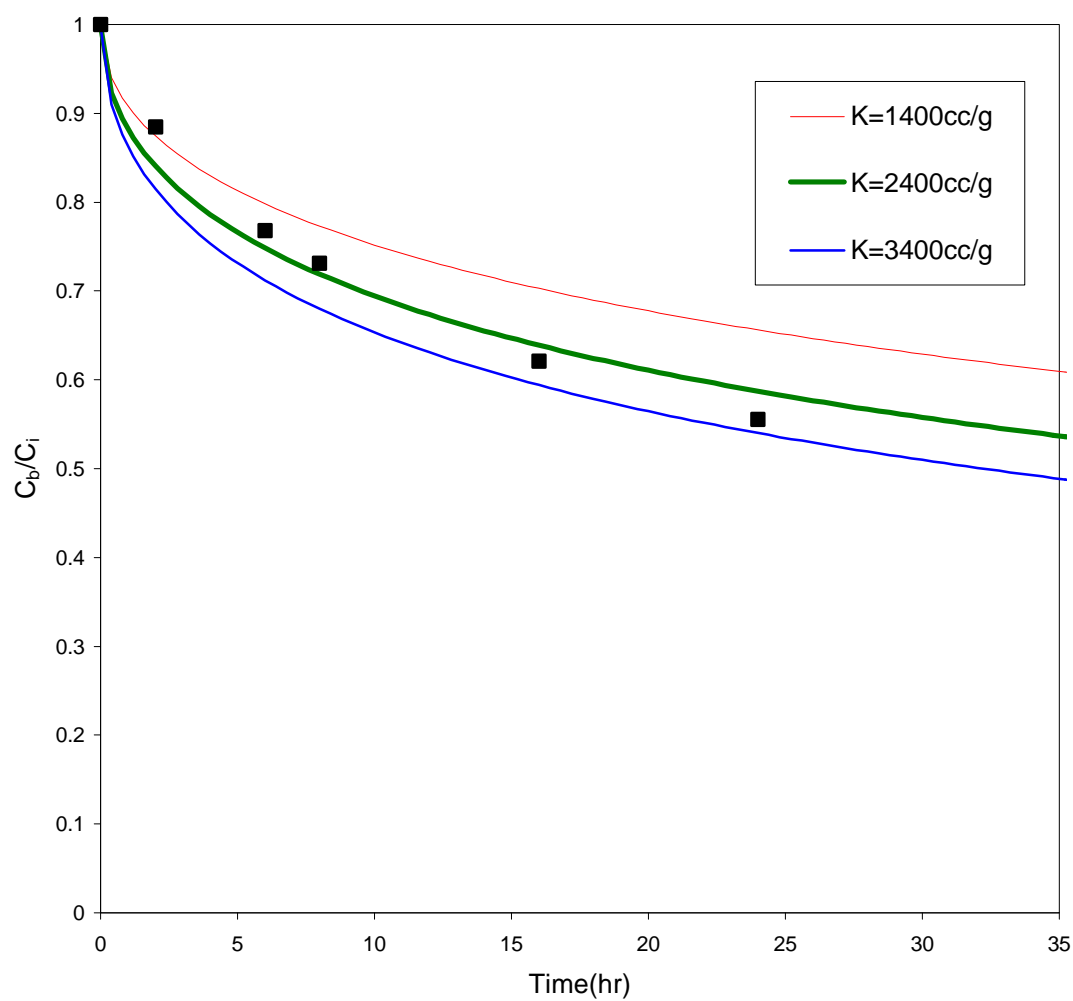


Figure 5. Comparison between experimental data and model simulation for the adsorptive uptake of P-AAD in toluene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=20^\circ\text{C}$)

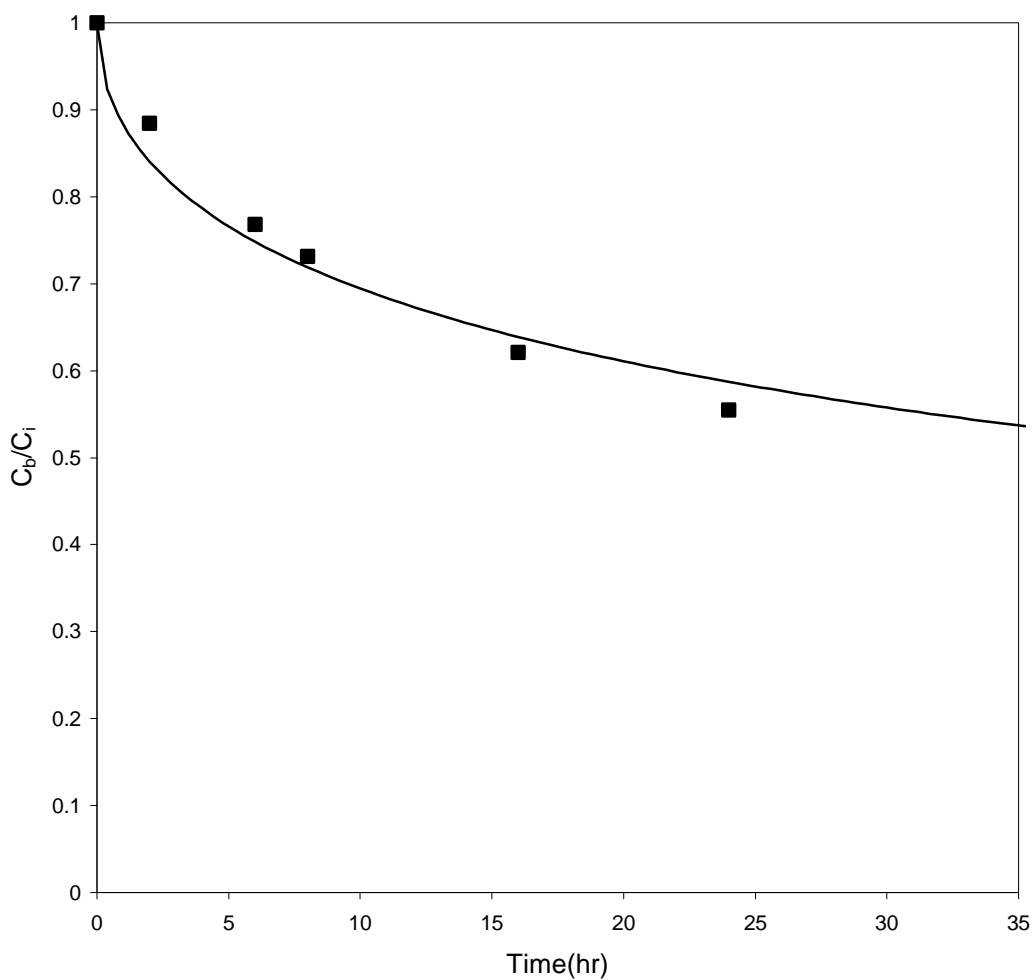


Figure 6. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of P-AAD in toluene on porous carbon catalyst (V=10ml, W=0.1g, T=20°C, K=2400cc/g)

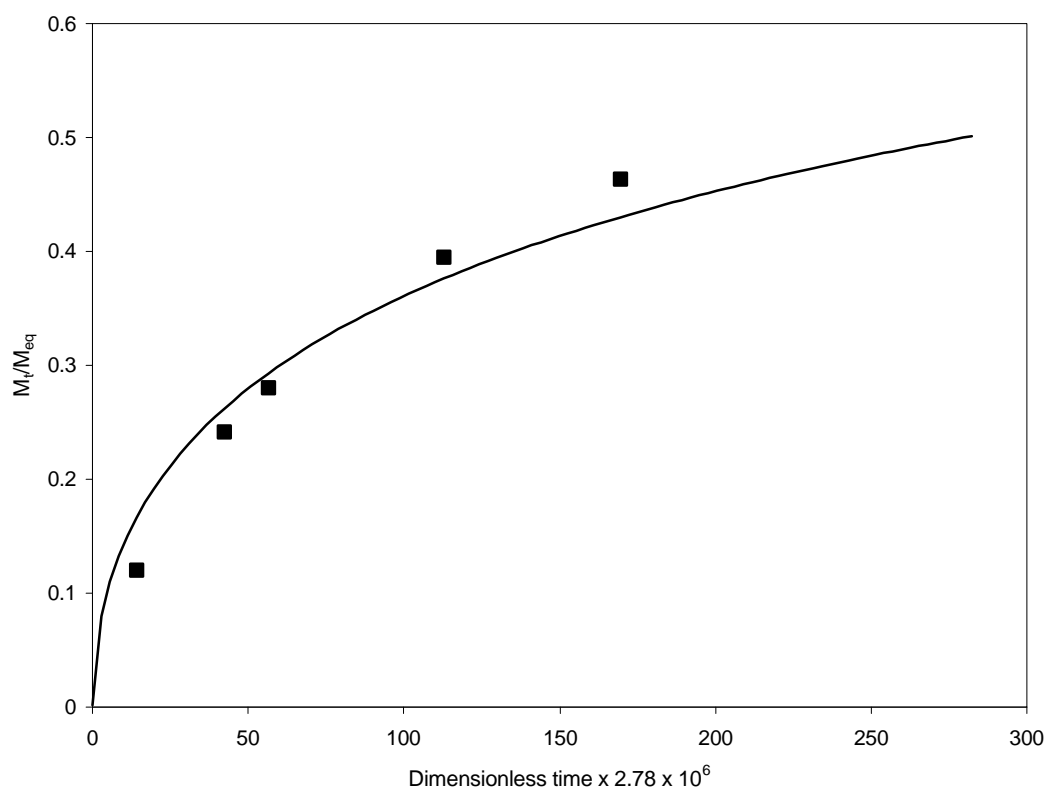


Figure 7. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of P-AAD in toluene on porous carbon catalyst (V=10ml, W=0.1g, T=20°C, K=2400cc/g)

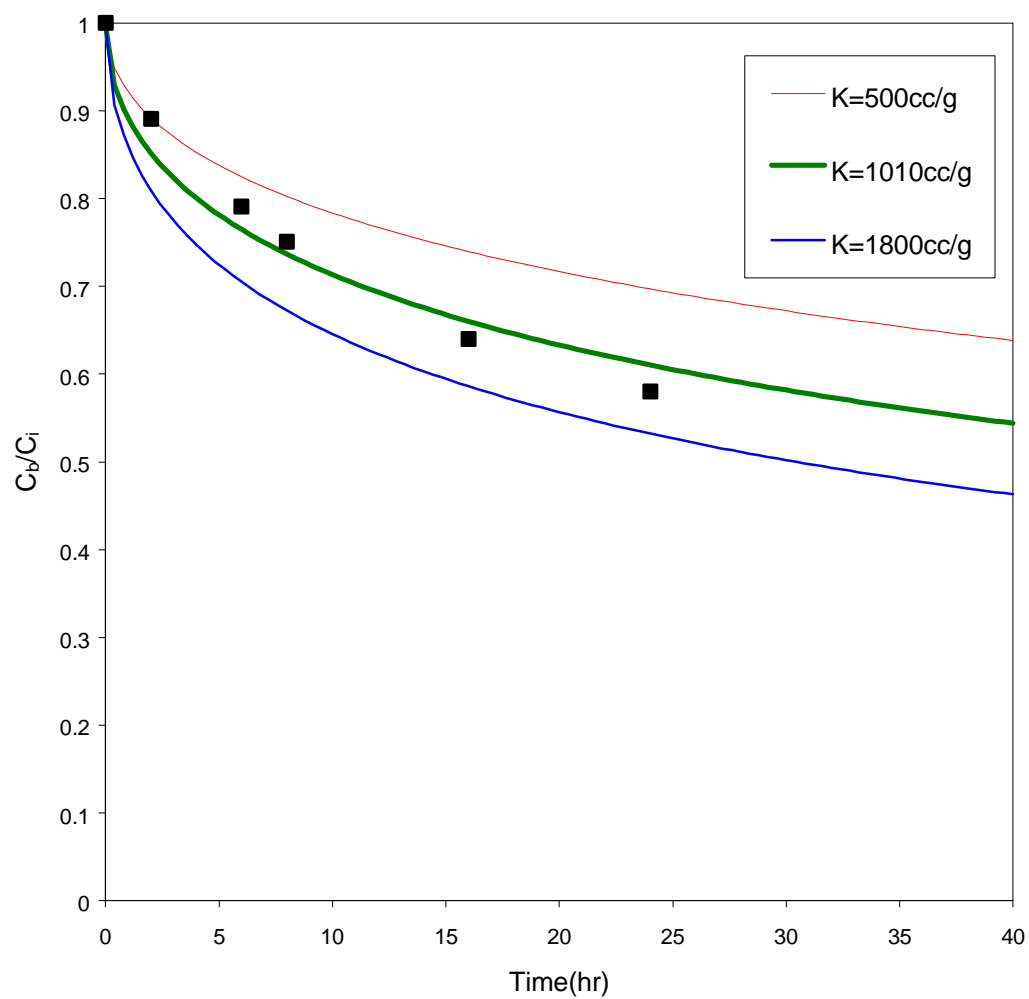


Figure 8. Comparison between experimental data and model simulation for the adsorptive uptake of P-AAD in toluene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=75^\circ\text{C}$)

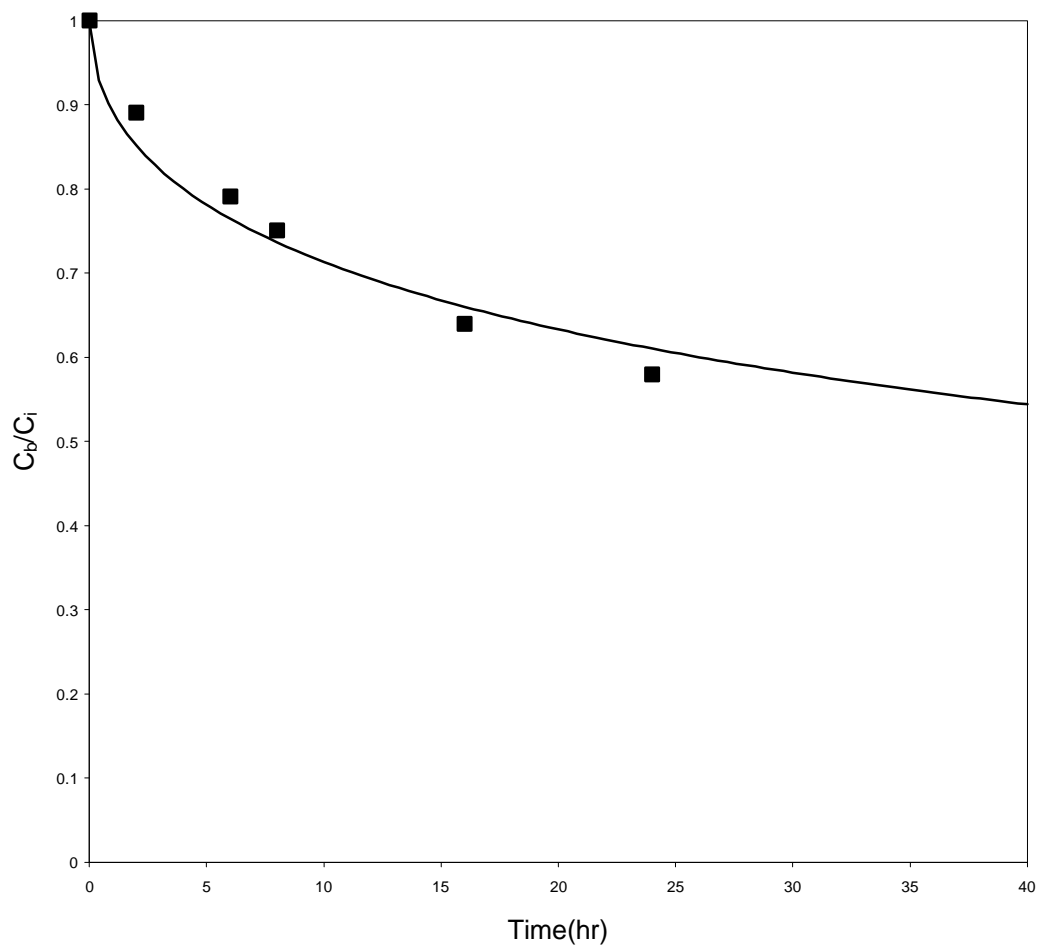


Figure 9. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of P-AAD in toluene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=75^\circ\text{C}$, $K=1010\text{cc/g}$)

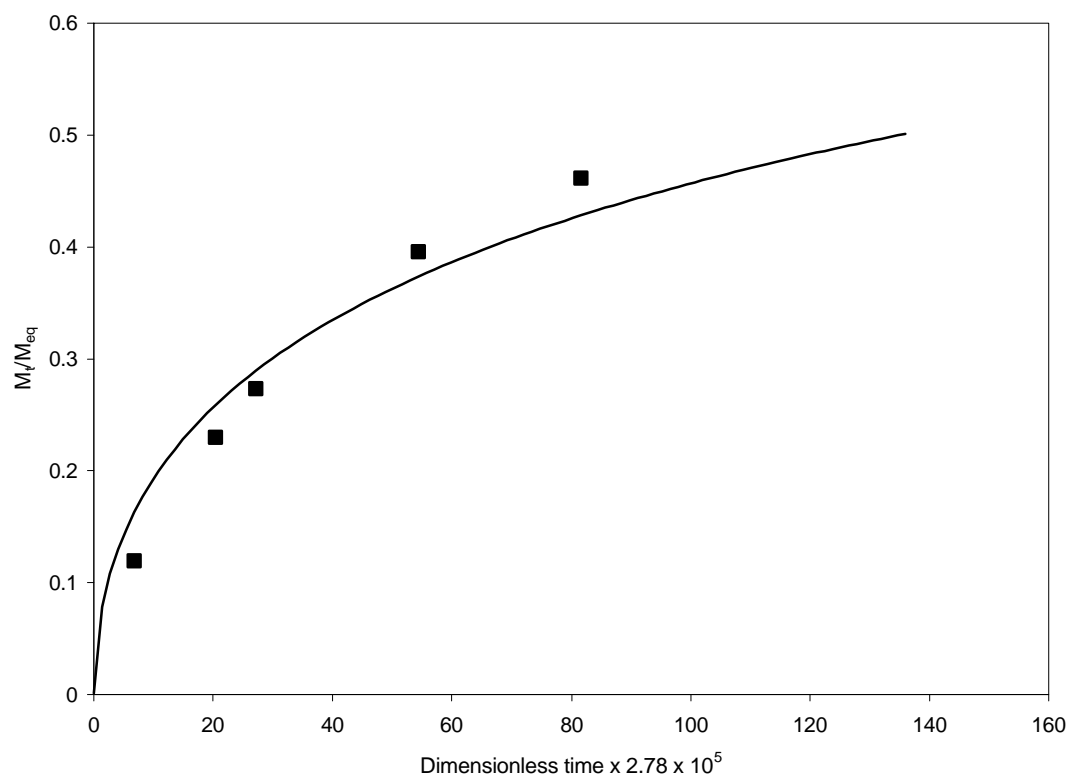


Figure 10. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of P-AAD in toluene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=75^\circ\text{C}$, $K=1010\text{cc/g}$)

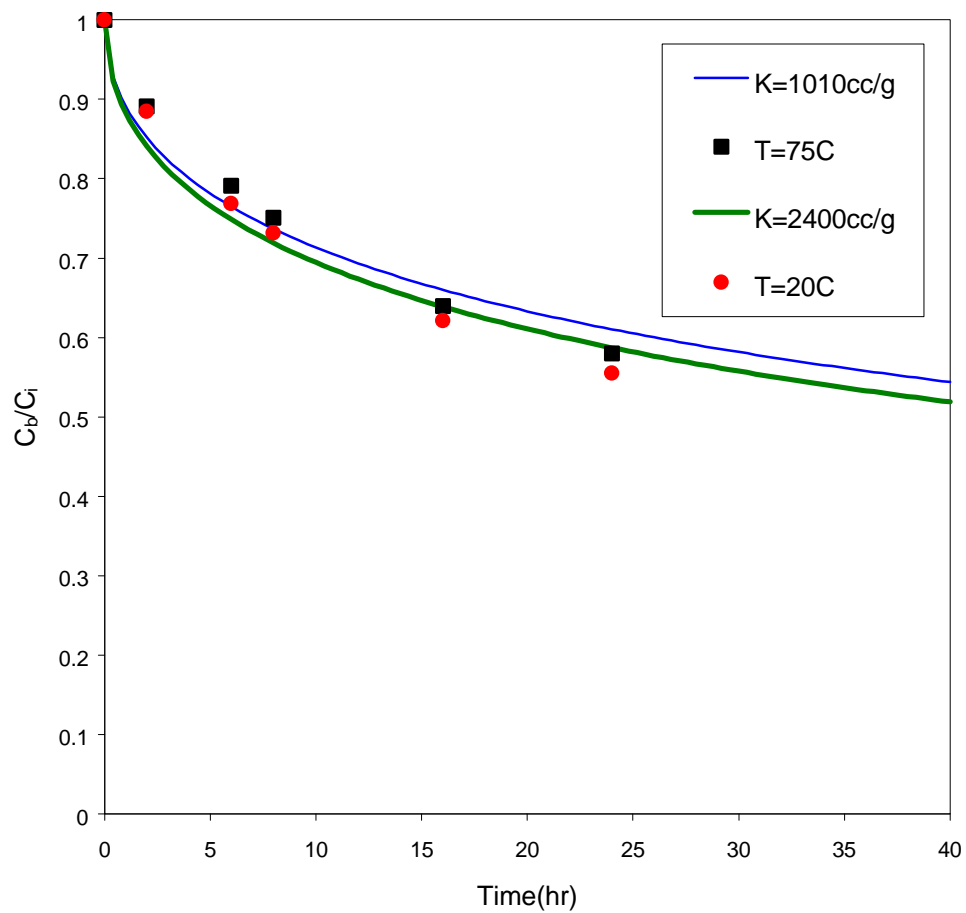


Figure 11. Effect of temperature on the adsorptive uptake of P-AAD in toluene on porous carbon catalyst (V/W =100cc/g)

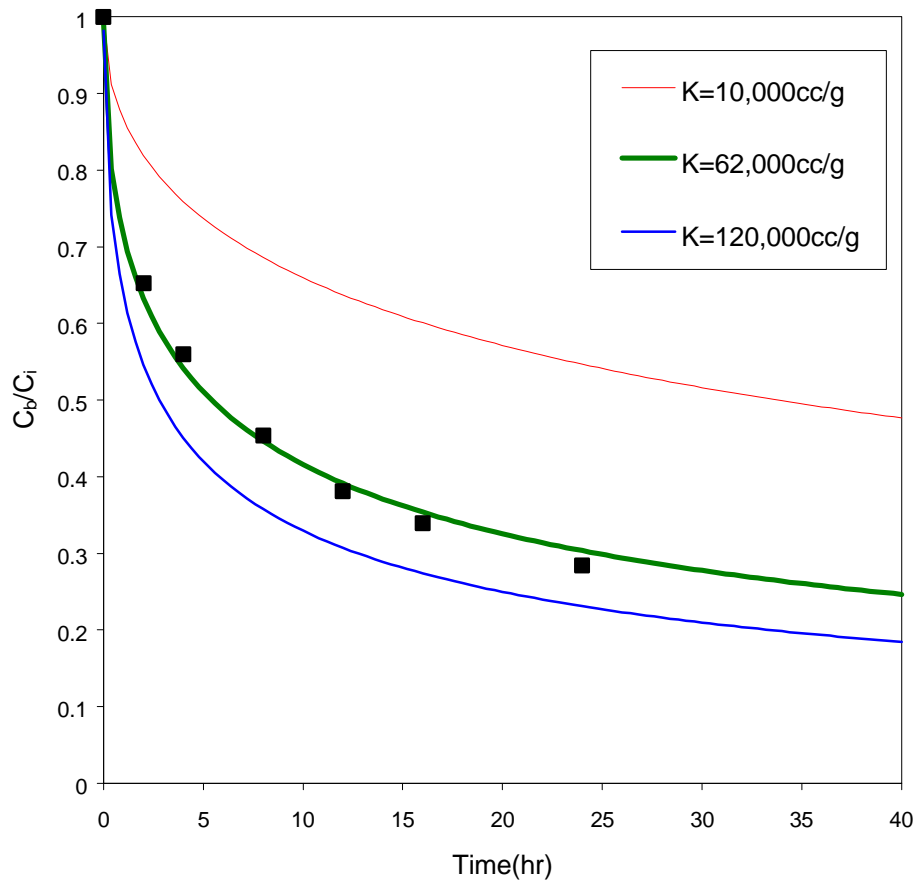


Figure 12. Comparison between experimental data and model simulation for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=100^\circ\text{C}$)

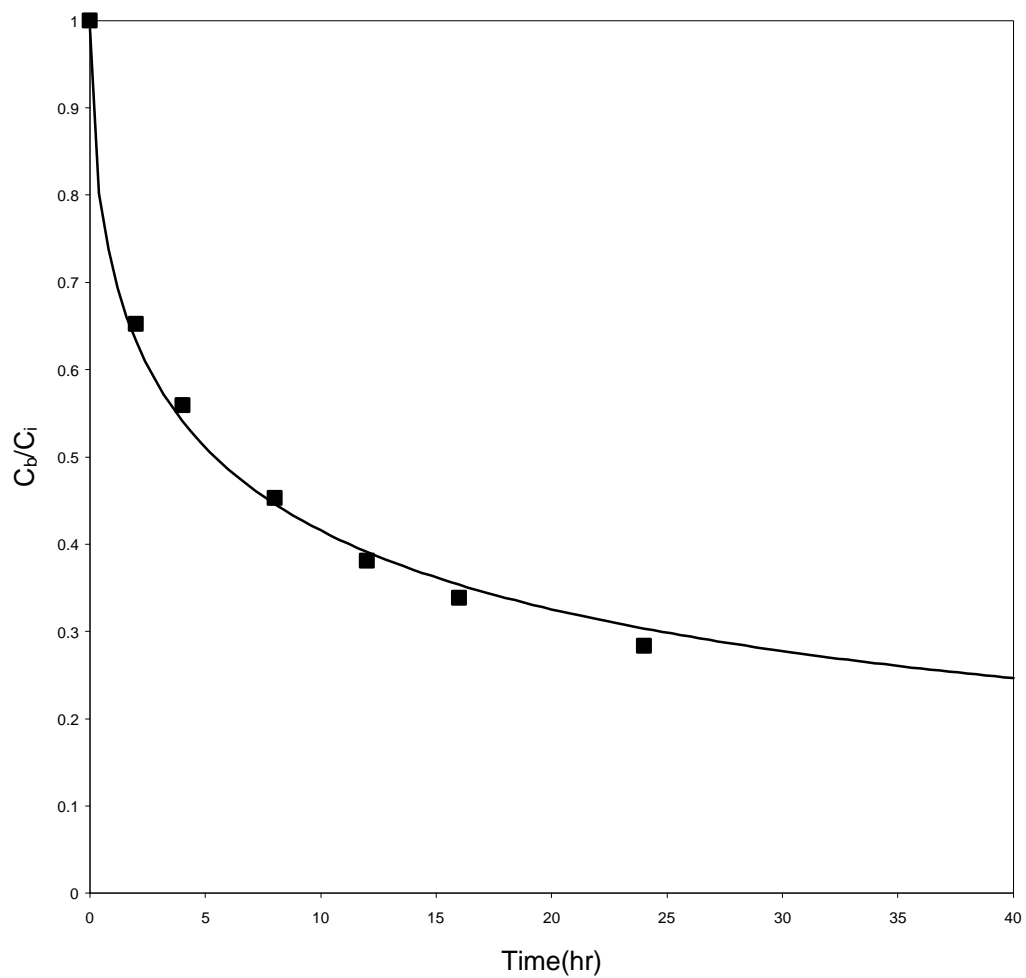


Figure 13. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=100^\circ\text{C}$, $K=6.2 \times 10^4 \text{cc/g}$)

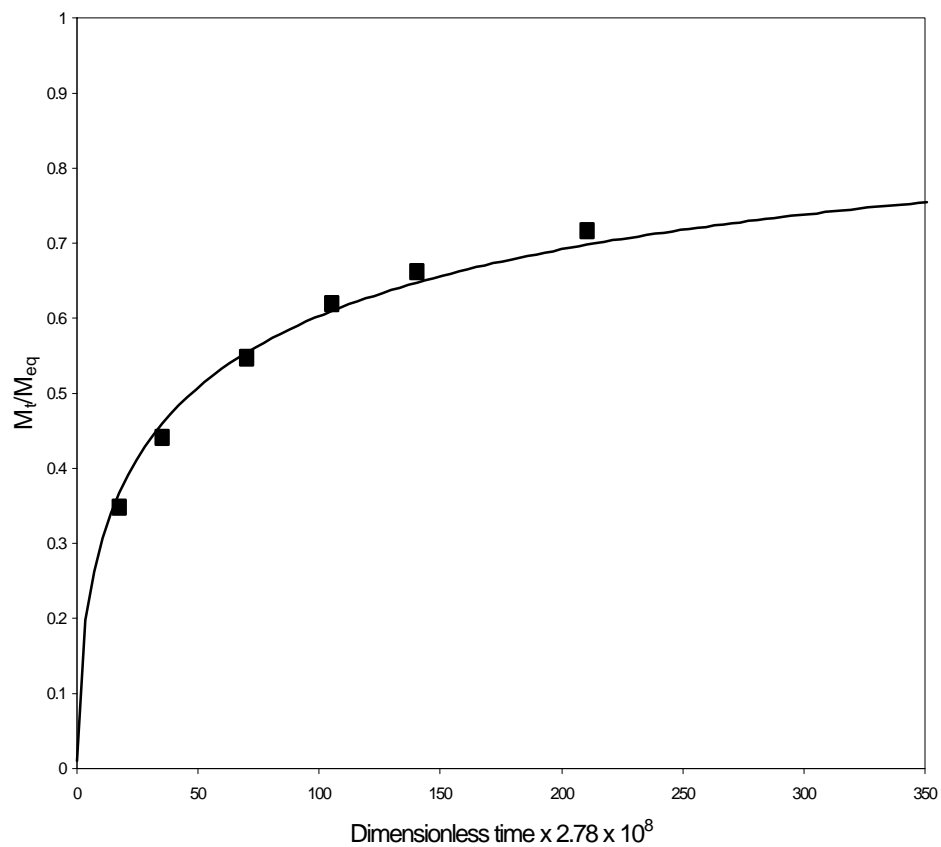


Figure 14. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=100^\circ\text{C}$, $K=6.2 \times 10^4\text{cc/g}$)

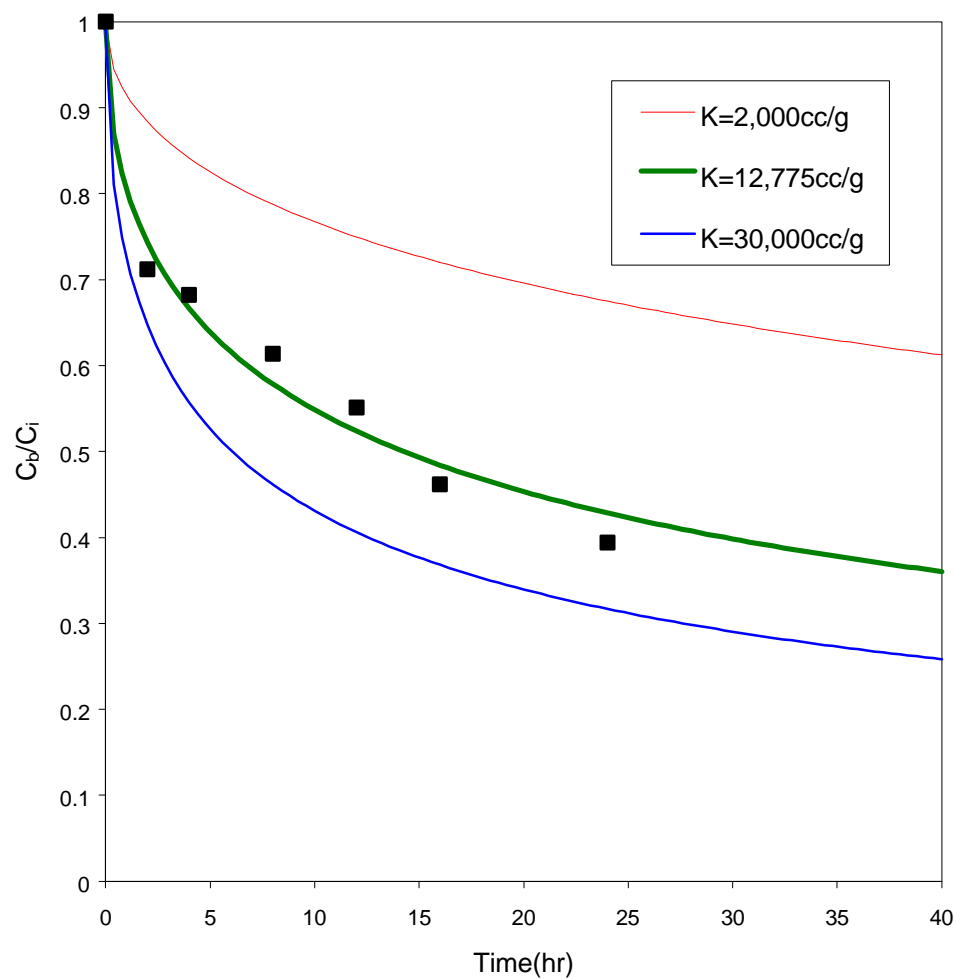


Figure 15. Comparison between experimental data and model simulation for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=150^\circ\text{C}$)

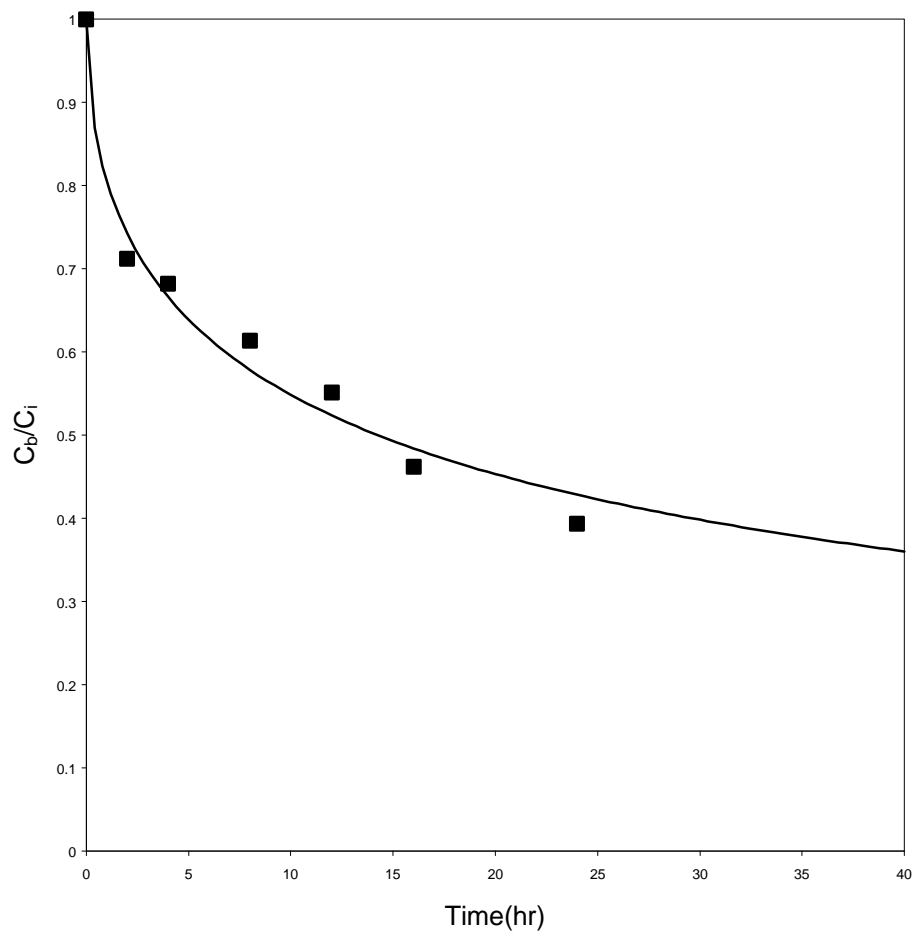


Figure 16. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=150^\circ\text{C}$, $K=12,775\text{cc/g}$)

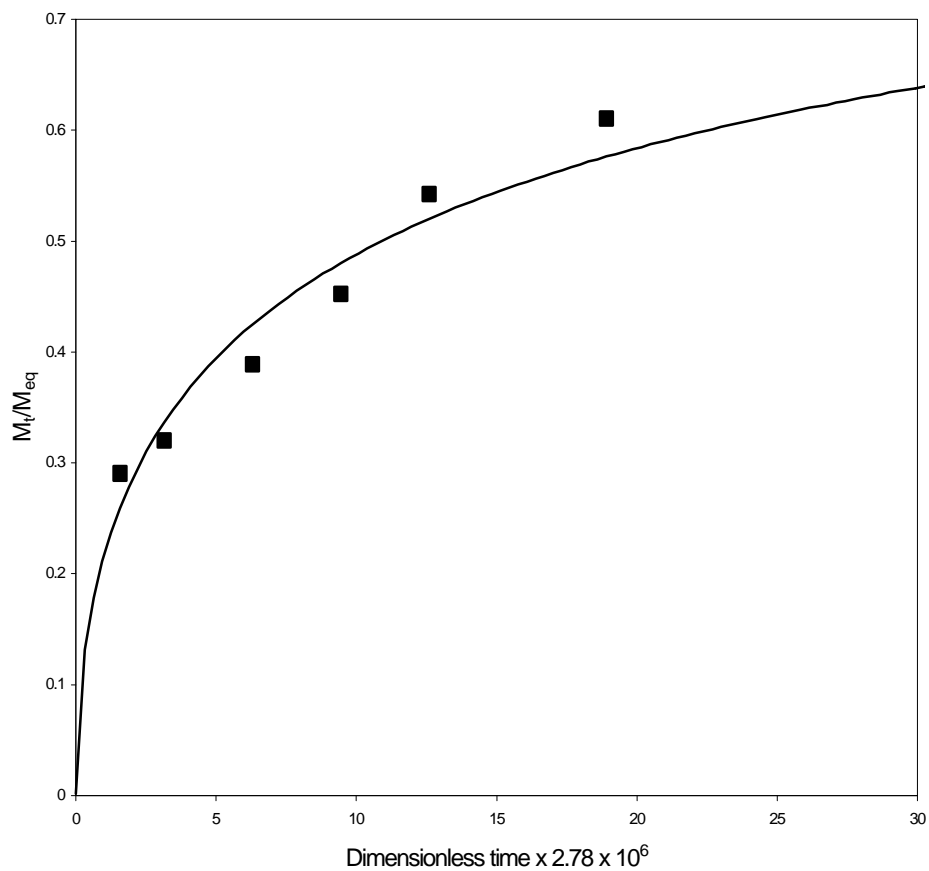


Figure 17. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=150^\circ\text{C}$, $K=12,775\text{cc/g}$)

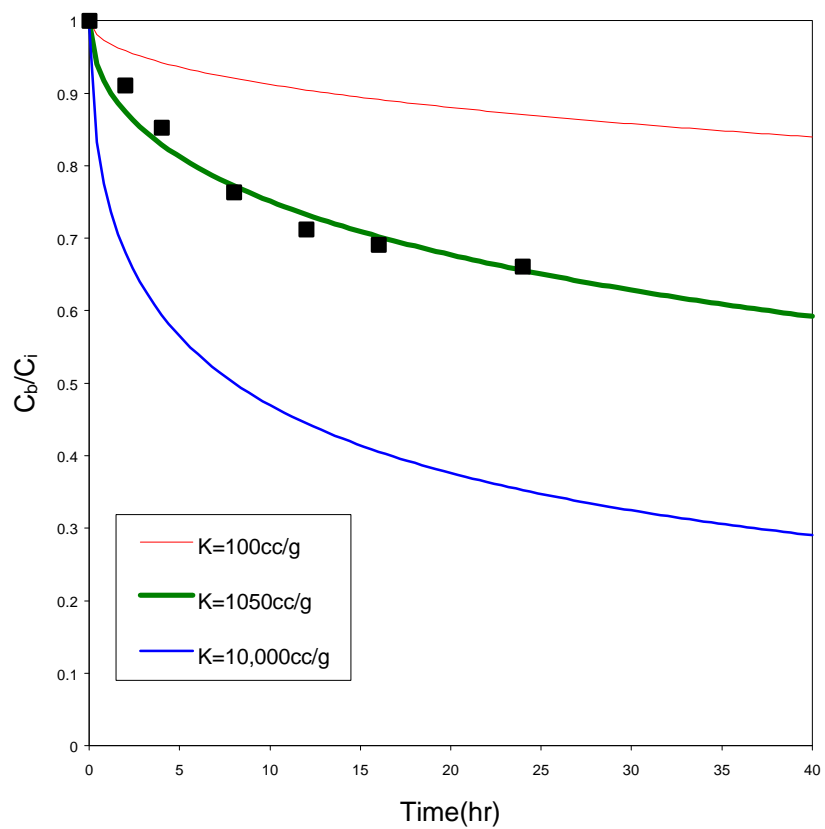


Figure 18. Comparison between experimental data and model simulation for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=250^\circ\text{C}$)

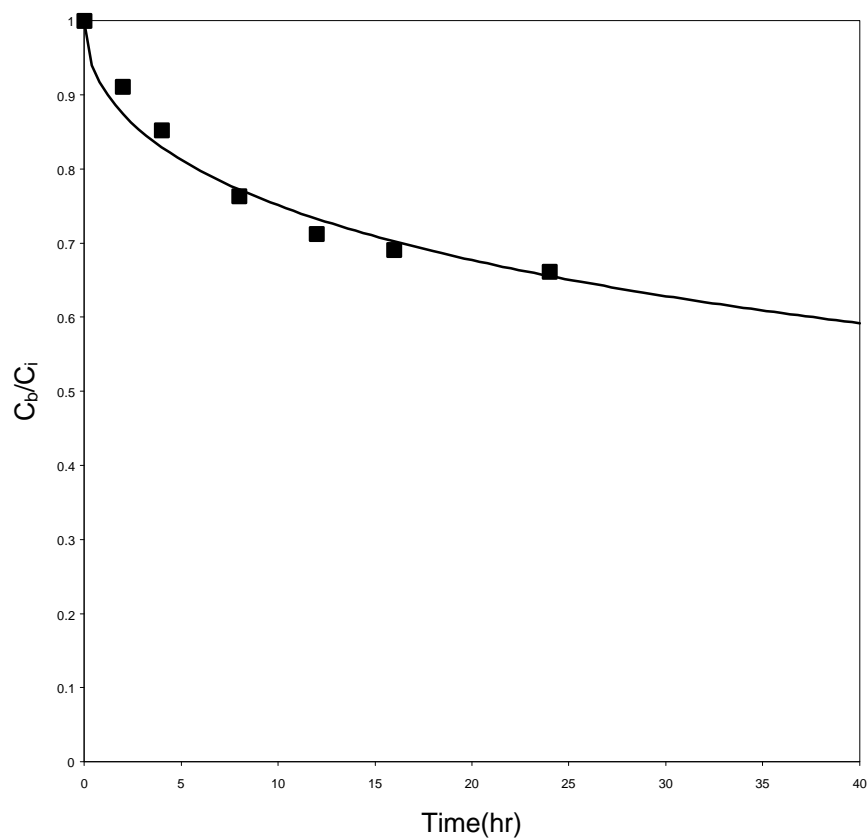


Figure 19. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=250^\circ\text{C}$, $K=1050\text{cc/g}$)

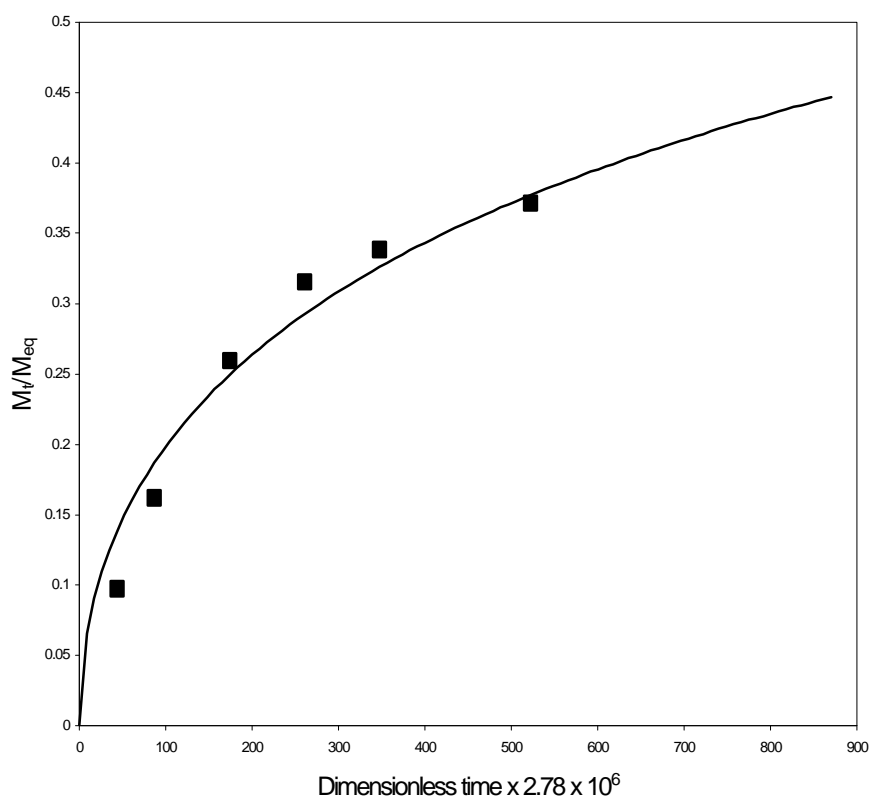


Figure 20. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst ($V=10\text{ml}$, $W=0.1\text{g}$, $T=250^\circ\text{C}$, $K=1050\text{cc/g}$)

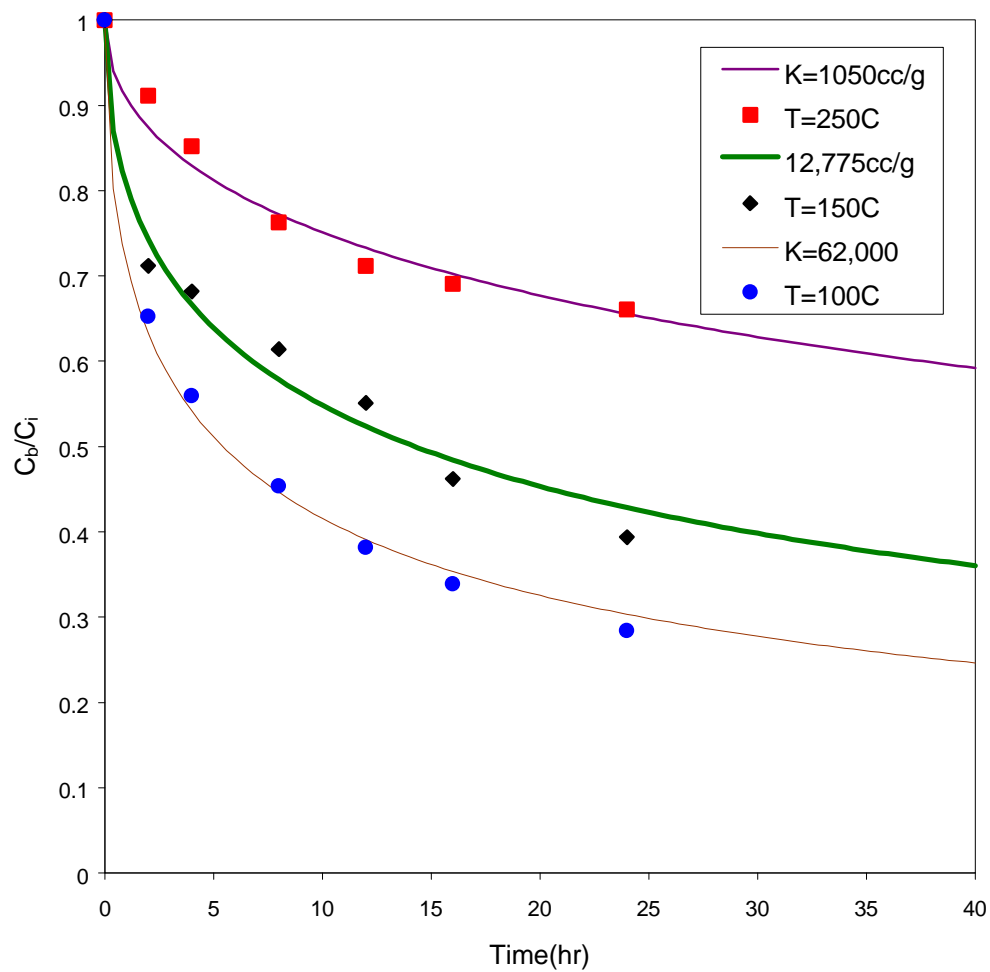


Figure 21. Effect of temperature on the adsorptive uptake of C-257K in 1-methylnaphthalene on porous carbon catalyst (V/W=100cc/g)

CONCLUSIONS

Experiments were performed in a microautoclave to study the diffusion controlled uptake of a coal asphaltene (C-257K) in toluene, a petroleum asphaltene (P-AAD) in toluene, and C-257K in 1-methylnaphthalene, onto a porous carbon catalyst substrate. As before, a C++ program was used to simulate data using the mathematical model which we had developed previously for diffusion controlled adsorption. A comparison between the experimental data and model simulated data showed that the mathematical model satisfactorily fitted the adsorptive diffusion of coal and petroleum asphaltenes onto the porous carbon. The adsorption constant for the P-AAD/toluene system decreased with increases in temperature from 20°C to 75°C. Similarly, the adsorption constant for the C-257K/1-methylnaphthalene system was found to decrease with increases in temperature. The adsorption constant for the C-257K/toluene system at 75°C was much higher than that of the P-AAD/toluene system at the same temperature. This fact suggest an apparent stronger adsorption of the coal asphaltenes on the surface of the carbon catalyst, as compared to the petroleum asphaltenes. This may be due to the increased functional groups on the coal asphaltenes, as compared to their petroleum counterparts.

In related work, several carbon catalyst supports were prepared in the laboratory and will be tested for their diffusional characteristics in asphaltene diffusion experiments during the next time period.

NOMENCLATURE

Letters

C_b	solute bath concentration, g/cm ³
C_i	initial solute bath concentration, 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
r_m	solute molecular size, cm
T	temperature, °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

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PLANNED WORK

In the next time period, it is expected that the current MS student, Mr. Ganesh Ramakrishnan will graduate. Prior to his graduation, Mr. Ramakrishnan will perform experiments for the diffusion controlled adsorptive uptake of the petroleum asphaltene onto porous carbon at higher temperatures, while a new student will perform investigations with a new carbon catalyst produced in this laboratory.

Correction: In the previous semi-annual report on this project, the dimensionless time values in Figures 4, 7, and 12 are too small by a factor of 3600 and should be corrected by multiplication by this factor.