

# SENSITIVITY ANALYSIS OF PLUG FLOW PORE SURFACE DIFFUSION MODEL I: FOR SINGLE COMPONENT

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**Abstract :** Adsorption of organic component on activated carbon is an interfacial phenomenon which is driven by concentration difference or gradient of solute at a phase boundary compared to the bulk solution. The used model to predict adsorption of organic component is plug flow pore surface diffusion model (PFPSDM). The sensitivity analysis was performed to determine which parameters have the greatest impact on the model results for a single component which can represent various organics. For the single component sensitivity analysis, the molecular weight was an important parameter. The breakthrough of the smaller molecular weight components was impacted more by backwashing. The SPDFR showed a significant impact on the breakthrough pattern. When surface diffusion was the dominant mechanism, high SPDFR, the breakthrough profile was sharper than when pore diffusion was dominant, low SPDFR. The adsorbability was an important parameter in determining the breakthrough pattern. As expected, the strongly adsorbable component showed the later breakthrough. Backwashing yielded earlier breakthrough for all single components examined.

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**Key Words :** GAC, Adsorption, numerical model, NOM, Freundlich isotherm

## INTRODUCTION

Adsorption of organic component on activated carbon is an interfacial phenomenon which is driven by concentration difference or gradient of solute at a phase boundary compared to the bulk solution. In the activated carbon adsorption, the interface is the pores or surfaces which exist outside or inside of the carbon particles. The pore consists of very complex channels of inside of the particles. Accordingly, an adsorbate should penetrate from bulk solution into the inner structure of activated carbon particles before it reaches an interfacial surface. Therefore, activated carbon adsorption is known as mass

transfer or transfer phenomena.

Once an adsorbate has diffused from the bulk solution to the surface of the adsorbent, it can either adsorb or diffuse to the inside of the adsorbent. The high internal surface area of the adsorbent causes a concentration gradient for the adsorbate, which is the driving force for the flux. The internal mass transfer step can proceed within the fluid void space contained within the pores, which is referred to as pore diffusion, or along the surface walls of the pores as adsorbed molecules, which is referred to as surface diffusion.<sup>1)</sup> Thus, the overall mass transfer incorporates two intraparticle mechanisms and one external mechanism, which can be used to describe the adsorption kinetics in a fixed bed adsorber.

There are many models to predict adsorption

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behaviors on activated carbon. Homogeneous surface diffusion model (HSDM) is one of the well known model to predict adsorption of organic components onto activated carbon. However, the HSDM does not consider the pore diffusion.

The other model to predict adsorption of organic component is plug flow pore surface diffusion model (PFPSDM). The model considers that the diffusion is divided into pore and surface diffusion. Therefore, the PFPSDM can predict adsorption behavior more precisely.

In this study, a sensitivity analysis was performed to determine which parameters have the greatest impact on the model results for a single component which can represent various organics. The parameters used in this study include: molecular weight, surface pore diffusion flux ratio (SPDFR), tortuosity ( $\tau$ ), adsorbability and backwashing frequency for a single component.

## MODEL DEVELOPMENT FOR THE PFPSDM

The equations describing the PFPSDM in a fixed bed adsorber are presented. The general equations are developed in this study in dimensional form; the dimensionless forms are described by Vaith.<sup>2,3)</sup> The assumptions incorporated into the PFPSDM are as follows: 1) the liquid phase flux is described by the linear driving force approximation, 2) the adsorption rate is very fast (local equilibrium), 3) the single component adsorption equilibrium is described by the single solute Freundlich isotherm equation, 4) surface and pore diffusion describe the intraparticle mass flux and are independent of concentration, 5) there are no solute-solute interactions in the diffusion process, 6) the adsorbent particle is spherical, 7) solute transport in the axial direction occurs by advective flow, and 8) there is no radial dispersion or channeling.

To derive the overall mass balance for single component in the fixed bed, a mass balance is written on a differential element in the bed. The adsorbate can be transferred into or out the

differential element by advection, dispersion, and diffusion. The mass balance can be expressed in mathematical terms as follows:

$$\begin{aligned} & \varepsilon v A [C(z, t) - C(z + \Delta z, t)] \Delta t \\ & - \varepsilon A D_e \left[ \frac{\partial C(z, t)}{\partial z} - \frac{\partial C(z + \Delta z, t)}{\partial z} \right] \Delta t \\ & = \varepsilon A [C(z, t + \Delta t) - C(z, t)] \\ & + \rho_a (1 - \varepsilon) A [q_{\text{avg}}(z, t + \Delta t) - q_{\text{avg}}(z, t)] \\ & \left[ + \frac{\varepsilon_p}{P_a} C_{p, \text{avg}}(z, t + \Delta t) - \frac{\varepsilon_p}{P_a} C_{p, \text{avg}}(z, t) \right] \Delta z \end{aligned} \quad (1)$$

in which,  $\varepsilon$  is the bed porosity;  $v$  is the interstitial velocity;  $\varepsilon_p$  is the void fraction of the pores within the adsorbent;  $A$  is the cross sectional area of the differential element;  $C(z, t)$  is the liquid phase concentration of the component;  $D_e$  is the axial eddy dispersivity based on the interstitial velocity of the component;  $\rho_a$  is the adsorbent density;  $q_{\text{avg}}(z, t)$  is the average adsorbent phase concentration of the component;  $C_{p, \text{avg}}$  is the average adsorbate concentration of the component in the adsorbent pores;  $z$  is the axial coordinate; and  $t$  is the elapsed time.

The average adsorbent phase concentration is given by;

$$q_{\text{avg}}(z, t) + \frac{\varepsilon_p}{\rho_a} C_{p, \text{avg}}(z, t) = \frac{3}{R^3} \int_0^R \left[ q(r, z, t) - \frac{\varepsilon_p}{\rho_a} C_p(r, z, t) \right] r^2 dr \quad (2)$$

in which,  $R$  is the radius of the adsorbent; and  $r$  is the radial coordinate.

Dividing Eq. 1 by  $A \Delta z \Delta t$  and taking the limits as  $\Delta z$  and  $\Delta t$  approach zero and substituting the Eq. 2 into Eq. 1 yield Eq. 3. Eq. 3 is the final form of the overall mass balance for component  $i$  in the fixed bed adsorber.

$$\begin{aligned} & -V \varepsilon \frac{dC(z, t)}{dz} + \varepsilon D_e \frac{d^2 C(z, t)}{dz^2} = \\ & \varepsilon \frac{dC(z, t)}{dt} + \frac{3 \rho_a (1 - \varepsilon)}{R^3} \frac{\partial}{\partial t} \int_0^R \\ & \left[ q(z, r, t) + \frac{\varepsilon_p}{\rho_a} C_p(r, z, t) \right] r^2 dr \end{aligned} \quad (3)$$

The dispersion term in Eq. 3 can be neglected based on initial model assumptions. Thus, Eq. 3 becomes a first order partial derivative with respect to  $z$ . In order to solve Eq. 3, one initial condition and one boundary condition are needed. The initial and boundary conditions are as follows:

$$C(0 \leq x \leq L, t = 0) = 0 \tag{4}$$

$$V[C_0 - C(z=L, t)] = \frac{\partial}{\partial t} \int_0^L [C(z, t) + \frac{3\rho_a(1-\epsilon)}{\epsilon R^3} \int_0^R [q(r, z, t) + \frac{\epsilon_p}{\rho_a} C_p(r, z, t) r^2 dr] dz \tag{5}$$

The liquid phase mass balance for the component is derived using the same differential element used in the previous development. The final form of the liquid phase mass balance for the component in the fixed bed adsorber is:

$$-v \frac{dC(z, t)}{dz} + D_c \frac{d^2C(z, t)}{dz^2} = \frac{dC(z, t)}{dt} + \frac{3\beta_L(1-\epsilon)}{R\epsilon} [C(z, t) - C_p(r=R, z, t)] \tag{6}$$

in which,  $C_p(r=R, z, t)$  is the adsorbate concentration of the component at the adsorbent surface and  $\beta_L$  is the external mass transfer coefficient. The final form of the intraparticle mass balance is given by Eq. 7.

$$\frac{1}{r^2} \frac{\partial}{\partial t} [r^2 D_s \frac{\partial q(r, z, t)}{\partial r} + r^2 \frac{D_p \epsilon_p}{\rho_a} \frac{\partial C_p(r, z, t)}{\partial r}] = \frac{\partial}{\partial t} [q(r, z, t) + \frac{\epsilon_p}{\rho_a} C_p(r, z, t)] \tag{7}$$

in which,  $D_s$  is the surface diffusion coefficient and  $D_p$  is the pore diffusion coefficient of the component. The initial condition for Eq. 7 is:

$$(q + \frac{\epsilon_p}{\rho_a} C_p)(0 \leq r \leq R, 0 \leq z \leq L, t = 0) = 0 \tag{8}$$

The following equations are the boundary conditions for Eq. 7.

$$\frac{\partial}{\partial r} [(q + \frac{\epsilon_p}{\rho_a} C_p)(r=0, 0 \leq z \leq L, t = 0)] = 0 \tag{9}$$

$$\frac{\partial}{\partial r} \int_0^R [q(r, z, t) + \frac{\epsilon_p}{\rho_a} C_p(r, z, t)] r^2 dr = \frac{k_f R^2}{\rho_a} [C(z, t) - C_p(r=R, z, t = 0)] \tag{10}$$

The nonlinear equation which couples the liquid and intraparticle mass balances is the Freundlich isotherm Eq. ;  $q=KC^n$ . The final result including the axial coordinate for the concentration of a single component is given by:<sup>4,5)</sup>

$$C_p(r, z, t) = \left( \frac{q(r, z, t)}{K} \right)^{\frac{1}{n}} \tag{11}$$

The pore diffusion coefficient is defined by Eq. 12 where  $\tau$  is the tortuosity.

$$D_p = \frac{D_L \epsilon_p}{\tau} \tag{12}$$

in which  $D_L$  is the liquid diffusivity. The surface diffusion coefficient,  $D_s$ , is a function of the empirically determined surface pore diffusion flux ratio (SPDFR).

$$D_s = \frac{D_L \epsilon_p C_0 \text{ SPDFR}}{KC_0^n} \tag{13}$$

When the SPDFR is much greater than 1.0 the dominant intraparticle mechanism is surface diffusion. When it is much less than 1.0, pore diffusion dominates. When the SPDFR is 1.0 there is no dominant intraparticle mechanism, i.e. surface diffusion and pore diffusion equally contribute.

The above equations, from Eq. 1 to 13, constitute the PFPSDM. A system of simultaneous partial differential equations is solved by converting the equations to a system of ordinary

differential equations using the method of orthogonal collocation and then integrating by the GEAR method using the subroutine DGEAR.<sup>6)</sup>

## BACKWASHING MODEL DEVELOPMENT

Unless a prefilter is used, it is common in practice to backwash fixed-bed adsorbers on a regular basis to reduce headloss due to the accumulation of solid particles. Backwashing can be conducted with treated or untreated water, the former is more commonly used in practice. However, backwashing can be detrimental to adsorber performance as it has been shown to lead to earlier breakthrough.<sup>7-9)</sup>

The liquid and solid phase mass balances for the model development for a backwashed adsorber are the same as those used in the PFPSDM. The only difference is in accounting for backwashing. When the bed is backwashed the adsorbent phase concentrations will be redistributed due to the mixing. Since the new distribution is not known, the simplest form is to assume that the bed is completely mixed during backwashing, yielding the same solid phase concentration at all depths. Given the particle size and density distribution found with commercially available GAC, backwashing a column in practice does not yield a total restratified bed, but results in a very similar particle distribution after each backwashing. Thus, the assumption of completely mixed bed after backwashing is a conservative approach. The solid phase concentrations are averaged axially for each radial coordinate. Therefore, after backwashing each axial coordinate will have the same radial concentra-

tion gradient. All solid phase concentrations at each radial position are set to the average concentration,  $q_i$ , calculated by Eq. 14.

$$q(r, z, t) = \frac{\int_0^L q(r, z, t) dz}{\int_0^L dz} \quad (14)$$

The liquid phase concentration after backwashing can be set to the influent concentration (untreated water) or to a zero concentration (treated water). The worst scenario would be to use untreated water. This would give the most conservative results. For this reason, the liquid phase concentration was set to the influent concentration as follows:

$$C(z, t) = C_0 \quad (15)$$

The model follows the adsorption equations until the next backwashing process is introduced.

## RESULTS AND DISCUSSION

The parameters examined and their starting values are listed in Table 1. Selected parameters were varied one at a time over a range of values to test the response of the model. The sensitivity analysis was simultaneously performed for both the adsorption and the backwashing models. To assess the relative importance of estimating the mass transfer parameters for the fixed bed adsorber, first the single component sensitivity analysis was conducted. The initial parameter values used were determined based on the most general situation; equal pore and surface diffusion fluxes, SPDFR=1.0; the diffu-

Table 1. Input Parameters and Initial Values for Sensitivity Analysis

C0	Tortuosity	SPDFR	K	n	MW*	BF*
mg/L	-	-	(mg/g)(L/mg) <sup>n</sup>	-	daltons	BV*
5.0	1.0	1.0	25	0.2	150	1000

MW\*: Molecular weight

BF\*: Backwashing frequency

BV\*: Bed volumes

sion path is equal to particle radius,  $\tau=1.0$ ; small molecules, MW=150; backwashing every 6.5 days for an adsorber with an 8 min EBCT, backwashing frequency (BF) of 1000 BV; K and n values of a well adsorbed compound, K=25 and n=0.2. The concentration and K values used in section were expressed in terms of dissolved organic carbon. An EBCT of 8 min. was used.

Before backwashing, there exists a solid phase concentration distribution in the bed, as well as a bulk liquid solute concentration distribution as shown in Figure 1. The solid phase concentration distribution within the adsorbent is a function of position in the bed. The bed is gradually exhausted from the top of the column to the bottom of the column without backwashing. However, after backwashing the mass transfer zone no longer exists because of com-

plete mixing of the adsorbent, in which the saturated adsorbent at the top of the column can be relocated to the bottom of the column. After backwashing, the adsorbate concentration in the liquid phase can be lower than that of the solid phase at the bottom of the column, because the adsorbate concentration in the liquid phase is reduced while passing through the bed. Generally, the backwashed column showed earlier breakthrough due to the reverse adsorbate concentration gradient from the adsorbent to liquid phase at the bottom of the column. The reverse concentration gradient occurred because saturated adsorbents from the top of the column were relocated to the bottom of the column after being completely mixed during backwashing, allowing desorption to take place. This desorption can occur when the adsorption is reversible.

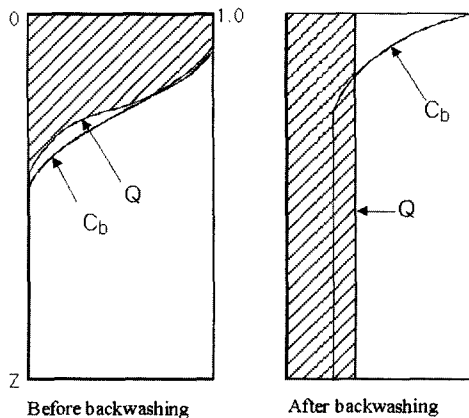


Figure 1. Comparison of saturated adsorbents distribution in the fixed-bed.

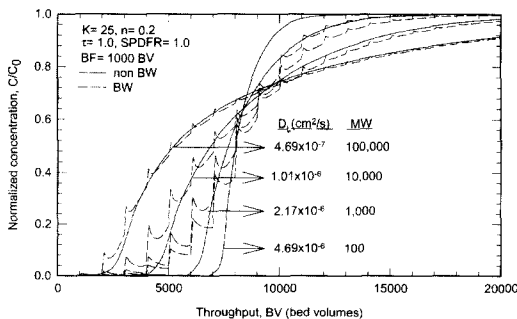


Figure 2. Impact of liquid diffusivity or molecular weight on single component breakthrough.

The model response to a change in the molecular weight (MW) or liquid diffusivity is shown Figure 2. The molecular weight was varied from 100 to 100,000. NOM has a molecular weight range of about 1,000 to 50,000. Liquid diffusivity is function of the molecular weight; lower molecular weight indicates faster liquid diffusivity. The liquid diffusivity coefficient was varied from  $4.69 \times 10^{-6}$  to  $4.69 \times 10^{-7}$  cm<sup>2</sup>/sec. In the PFPSDM, the liquid diffusivity affects both the pore and surface diffusion coefficients. A higher liquid diffusivity results in larger pore and surface diffusion coefficients. Therefore, smaller molecular weight components are transported more quickly through the boundary layer and in the particle compared to the MW components. The lowest MW compound showed a very sharp breakthrough curve. As the MW was increased, the shape of the breakthrough curve to 60 percent breakthrough was broader and indicated earlier breakthrough. The impact of varying the MW was similar for the backwashing model predictions. However, backwashing had a much greater impact on the breakthrough of the smaller MW components, as it resulted in an earlier breakthrough compared to that of the non-backwashed column. This was due to faster diffusivities of the smaller MW

compounds, which allowed them to quickly diffuse out of the GAC after backwashing. The impact of backwashing decreased as the MW was increased.

Figure 3 shows the impact of the SPDFR on breakthrough. When surface diffusion dominates,  $SPDFR > 1$ , the breakthrough pattern is sharper than when pore diffusion dominates,  $SPDFR < 1$ . Similar trends are seen with the backwashing model prediction, but backwashing always yielded earlier breakthrough for a given SPDFR. The impact of the tortuosity is shown in Figure 4. The tortuosity was varied from 1.0 to 10.0. The pore diffusion coefficient is impacted by the tortuosity as shown by Eq. 12. Varying the tortuosity in this range did not show as large an impact as the SPDFR for both column simulations. At 10 percent breakthrough the backwashed column showed about 33 percent earlier breakthrough. However, there was no significant

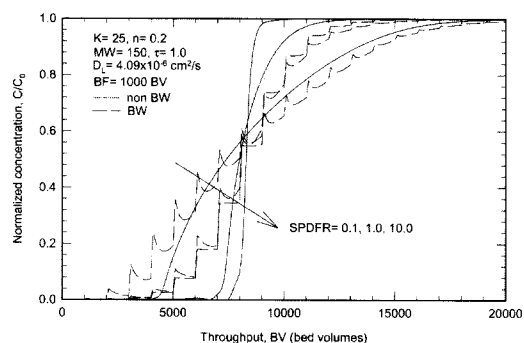


Figure 3. Impact of surface pore diffusion flux ratio on single component breakthrough.

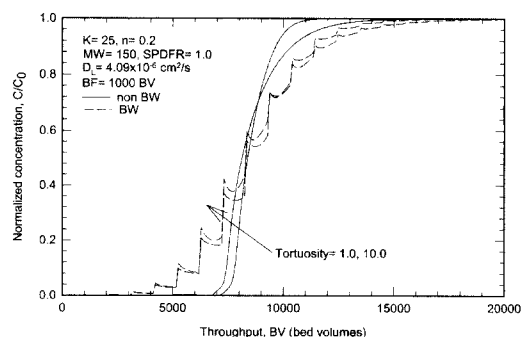


Figure 4. Impact of tortuosity on single component breakthrough.

difference at 50 percent breakthrough.

Figure 5 shows the impact of adsorbability and backwashing on the breakthrough. Each  $K$  value represents a common synthetic organic compound in terms of dissolved organic carbon. As expected, the weakly adsorbable component represented by dibromochloromethane,  $K=11$ , showed earlier breakthrough compared to the other two components. The impact of backwashing was very similar over the range of adsorbabilities examined. The backwashed column showed at most a 33 percent earlier breakthrough compared to that of the non-backwashed column at 10 percent breakthrough, while backwashing did not show any significant impact on the breakthrough pattern at 50 percent breakthrough.

The model response to a change in backwashing frequency is shown Figure 6. The backwashing frequency was varied from 300 to 5,000 BV, which represents backwashing every 2 to

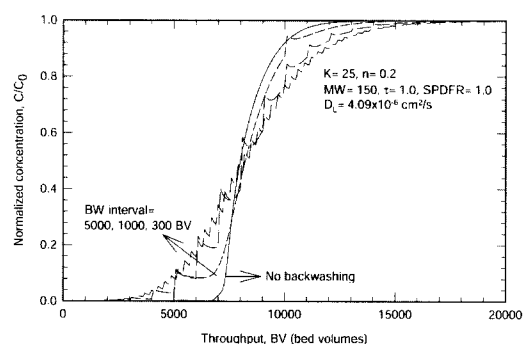


Figure 5. Impact of adsorbability on single component breakthrough.

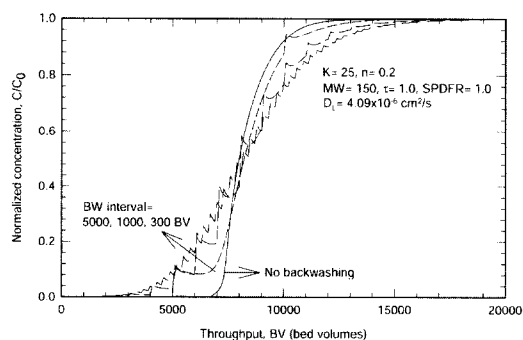


Figure 6. Impact of backwashing frequency on single component breakthrough.

30 days for an 8 min EBCT column. Even backwashing at 30 days intervals (BF= 5000 BV) impacted the breakthrough curve for this K values with a 50 percent breakthrough at 8000 BV. More frequent backwashing resulted in earlier breakthrough at 10 percent breakthrough, however there was no significant effect at 50 percent breakthrough. More frequent backwashing showed less impact of backwashing at each backwashing occurrence, because the less saturated adsorbent was relocated to the bottom of the column and less desorption occurred due to the concentration gradient. When the column is backwashed every 50 to 100 BV or more often, the column will behave like a fluidized bed, which means that the mass transfer zone will not exist in the column.

## CONCLUSIONS

For the single component sensitivity analysis, the molecular weight was an important parameter. It had a great impact on the single component breakthrough pattern because the low molecular weight compounds had faster liquid diffusivities. The breakthrough of the smaller molecular weight components was impacted more by backwashing. Because of their faster diffusivity the compound could diffuse out of the adsorbent after backwashing and appear in the effluent. The SPDFR showed a significant impact on the breakthrough pattern. When surface diffusion was the dominant mechanism, high SPDFR, the breakthrough profile was sharper than when pore diffusion was dominant, low SPDFR. Tortuosity was not an important parameter based on the range examined. The adsorbability was an important parameter in determining the breakthrough pattern. As expected, the strongly adsorbable component showed the later breakthrough. Backwashing yielded earlier breakthrough for all single components examined. The more frequent backwashing showed the wider breakthrough pattern.

## ACKNOWLEDGMENT

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