

## **Parameter Evaluation and Statistical Validation of Transport Parameters in Porous Media**

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### **INTRODUCTION**

The rational design and modeling of any process requires sound mathematical models and experimentally-based estimates of model parameters. Models which are good representations of the physical phenomena alleviate extensive experimentation, thus saving time and expense (Magbanua et al., 1998). Further, mathematical modeling is an extremely powerful tool for providing insight into the underlying mechanisms associated with complex process phenomena. In this paper, we first discuss some general classes of mathematical models. Next, we present the methods of parameter estimation and statistical validation. The application of these principles to develop and validate the parameters for a specific experimental system is then presented. The parameters in this modeling study represent those describing the flow through a one-dimensional reactor packed with porous beads.

#### **Classes of mathematical models**

Mathematical models can be grouped into two broad categories: (1) Phenomenological, and (2) Empirical. Phenomenological models, which are sometimes referred to as deterministic or first-principle models, are based on mathematical descriptions of the underlying physics and chemistry of the process. Empirical models, on the other hand, are trial-and-error methods based on intuition and experience (Simutis et al., 1997). Such empirical models are

developed by mapping the data with suitable functional forms, and adjusting various model parameters to best fit the data. These functional forms are often polynomial expressions whose coefficients are determined by regression of the available data. In the past few years, techniques such as neural networks have been demonstrated to empirically fit functional relationships between input and output data (Savkovic-Stevanovic, 1994).

Phenomenological models are always desirable since the predictions are generally valid over a greater range of operating conditions. However, the disadvantages of such models are that they tend to become increasingly complicated and computationally intensive, and also require *a priori* knowledge of the process phenomena. Empirical models, on the other hand, are easier to develop, because they are "black box" models, which when presented with input data, will output a response. The black box is tuned correctly to interpret input data through a process of calibration to determine the model parameters. The predictions of empirical models are suspect outside the range of the calibration data. These models are usually capable of handling complex and nonlinear problems with relatively little computational effort and time. Thus, the use of empirical models reduces the engineering effort in model development (Zannetti, 1990).

A first-principles model should always be the first choice if one is available or is possible to develop. Empirical models are useful to develop when data is

available over a broad range of experimental conditions and where a physical understanding of the system does not exist or is tedious to incorporate into mathematical descriptions. In general, the use of a first-principles model can provide a more sound basis than an empirical model.

#### **Parameter evaluation and model validation**

Regardless of whether the model is phenomenological or empirical, model development involves a determination of the "best fit" estimates of the model parameters. The observed differences between the model and experimental data are used to further improve the model until the desired accuracy is obtained (Brass et al., 1997). This process is accomplished by adjusting the model parameters to minimize an appropriate error criterion such as sum of squared errors. Regression based models commonly use criteria such as the regression coefficient, correlation coefficient, and root mean squared error to determine the goodness of fit between the model and data. Deterministic models require a user-defined quantitative criterion formulated by means of an objective function. Once an objective function is formulated, a suitable solution technique must be chosen. The solution procedures of deterministic models are usually more complex. In some instances, analytical solutions are available, in which case spreadsheets can be employed to determine optimal values of the parameters. Where analytical solutions are not available, numerical optimization procedures need to be employed to obtain "best fit" values of the model parameters. For optimization of single variables, search techniques can be used, while for multi-dimensional problems, it is necessary to use constrained or unconstrained optimization techniques.

Once the model parameters are determined, then the model should be verified and validated. In the verification step, the solution of the model is compared against an established solution to ensure that the equations have been implemented correctly (Natake, 1994). In this step, the model predictions can be compared to an analytical solution, or solutions of previously published work.

The purpose of validation is to assess if the model is demonstrated to be good enough for prediction purposes. Several methods have been employed for model validation. Some modelers have compared the model predictions with independent data, i.e., data on which the model parameters were not developed, and used "eyeballing" to determine the goodness of fit of the model. In fact, validation of

mathematical models in practice has relied heavily on the visual comparison between the data and corresponding model calculations (Butterfield, 1990). At this stage, more stringent criteria such as sum of squared errors between model predictions and the test data can be used to determine the goodness of fit.

An alternative method of validating model parameters is by using statistical experimental designs. Data from experiments over a broad range of conditions can be used to obtain the model parameters. Once the model parameters are obtained, the validation can be accomplished by statistical analysis of variance (ANOVA). If the parameters are determined to be statistically the "same" over the entire range of experimental conditions, then the model is more universally applicable. If the parameters statistically different for various experimental conditions, then caution must be exercised in the using predictions of the model for changing experimental conditions.

In some instances, although there may be a statistical difference between the model parameters obtained for various experimental conditions, the practical implications of using the parameter estimates from one set of conditions to another might be inconsequential. In other words, the user must search for "practical significance" in the validation results if the results of ANOVA suggest "statistical" significance.

#### **DETERMINATION OF TRANSPORT PARAMETERS IN A POROUS MEDIUM**

An application of parameter estimation is presented for the case of a flow through columnar reactor, which is packed with porous Bio-Sep™ beads. Our interest is to reduce selenite, a hazardous and soluble form of selenium, to elemental selenium, which is insoluble and non-hazardous. The beads are manufactured by DuPont and have the ability to house relatively high numbers of bacteria inside the macropore structure (Camp et al., 1994). These beads have shown promise in reactor systems in which contaminant concentrations are reduced economically (Turick et al., 1997).

In the system modeled, contaminated water is pumped through a columnar reactor. The soluble contaminant diffuses into the beads, where the bacteria convert the contaminant to non-toxic forms and immobilize the product. Conceptually, this treatment methodology is attractive, because it not only converts the contaminant to non-toxic forms, but also separates it from the effluent stream. If

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designed suitably, such a treatment system can be used to produce "clean" water from the effluent of the column. In order to suitably design and subsequently control the performance of a reactor system utilizing Bio-Sep™ beads, it is essential that the mechanisms of mass transport and reaction of various species flowing through the column be understood. The first step in the development of such a mathematical model is the determination of the flow parameters. The purpose of this work was therefore to determine these flow parameters based on the mass transport mechanisms of dispersion and mass transfer into the beads. By using residence time distribution of various ionic species, the dispersion and mass transfer coefficients were estimated.

### Experimental design, operation and analysis

Two sets of experiments were designed:

- The first series of experiments was designed to estimate the dispersion coefficient and porosity of the bed. In these experiments, the beads were coated with an epoxy polymer to prevent mass transfer of species into and out of the porous beads.
- The second series of experiments was based on a statistical experimental design, and the data was used to estimate the mass transfer coefficients with known values of dispersion and porosity from the previous experiments. In this case, uncoated beads were used.

A statistical experimental design with various ionic species was used to estimate the mass transfer coefficient. Six different ionic species – acetate, chloride, nitrite, nitrate, phosphate and selenite – were used in the experiments. Duplicate experiments were conducted so that an analysis of variance could be performed to determine the homogeneity of parameters for the various ionic species. The transport characteristics of acetate, nitrate and nitrite were of interest because these species are used as nutrients in our treatment of contaminated water. The choice of selenite was natural as it is the form of selenium that was to be studied in our subsequent experiments. Chloride and phosphate were used as they are present in our simulated wastewater medium. Chloride is also non-interactive and is widely used in tracer studies to determine residence time distributions. The liquid medium pumped through the column had the following composition: Acetate (200 mg/L), chloride

(200 mg/L), nitrite (100 mg/L), nitrate (150 mg/L), phosphate (600 mg/L) and selenite (50 mg/L).

A glass columnar reactor was used in all the experiments. The reactor was 2.5-cm in diameter and 21-cm in height. Initially the reactor was packed with the Bio-Sep™ beads. The coated beads were prepared by applying an enamel paint dissolved in toluene and isobutyl ketone using an aerosol spray.

The anion concentrations were measured using a Dionex DX 500 ion chromatograph, equipped with a CD20 conductivity detector. A 4 mm AS12 column, protected by a 4 mm AG12 guard column was used for the anion separation. The eluent used was a 40% solution of 2.1 mM  $\text{Na}_2\text{CO}_3$  and 0.8 mM  $\text{NaHCO}_3$  in nanopure water.

Selenite concentration was measured on a Thermo Jarrell Ash Ion Coupled Argon Plasma (ICAP) spectrophotometer, Model 61. A two-point calibration was performed prior to sample analysis. The calibration consisted of a blank (0 ppm selenite) and a 50 ppm selenite sample in the medium identical to that used in our experiments. An Eldex HPLC pump (Model number 120-8) was used to deliver eluent to the column. The data obtained with the use of this system was analyzed using PeakFit™ version 4.1 (Jandel Scientific).

### Mathematical model development

First, an empirical model was fit to the data to describe the flow through the reactor. PROC REG in SAS™ was used to fit various polynomial expressions to the experimental data and the regression coefficient was noted. Presented in Figure 1 is the fit of the "best" two polynomial expressions on the residence time distribution data for chloride on the coated beads. The regression coefficients for the third order polynomial fit was 0.8635, while that for the fourth order fit was 0.9627. Although a good fit is obtained, there is no physical significance for the polynomial coefficients. Also, the curves fit by the model predict negative values of the outlet concentration for the first few minutes, which is physically impossible. Although a suitable curve fit by an empirical model is easily accomplished, the use of such a model is not desirable in this instance due to its inadequate description of the experimental data.

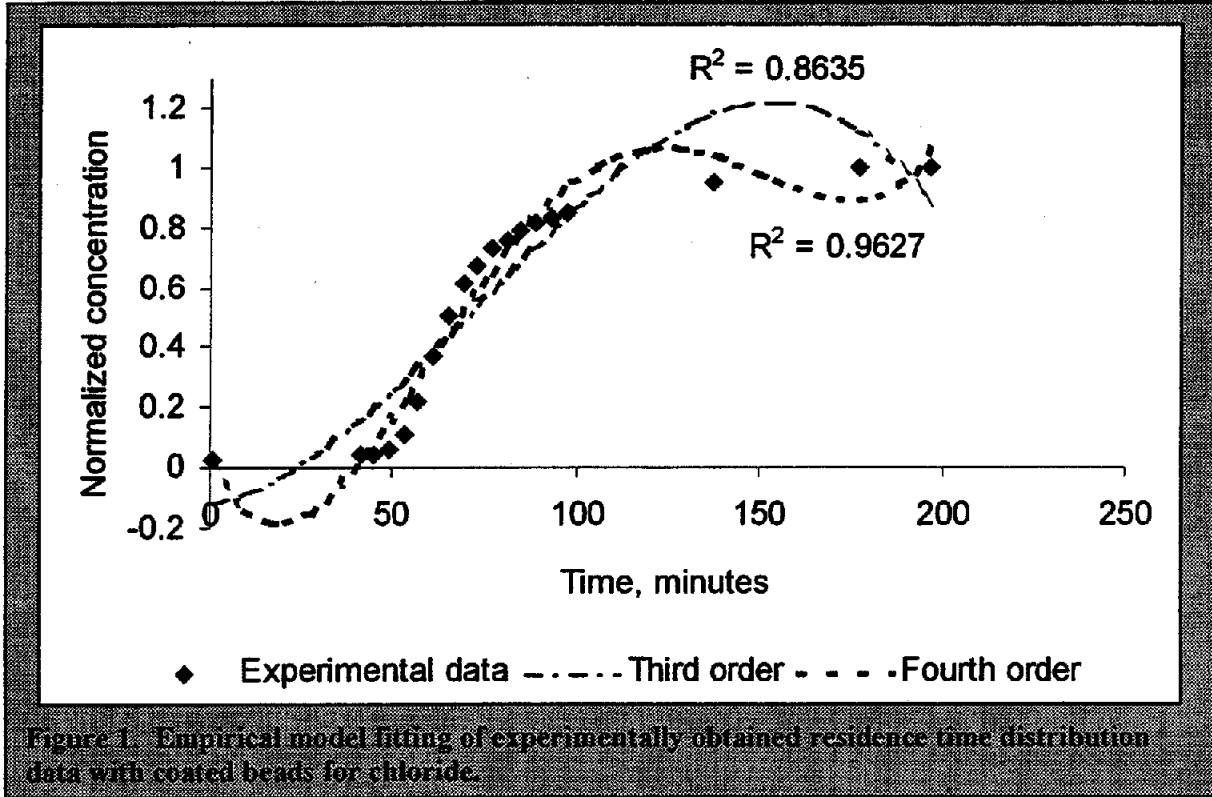
A phenomenological model was used to describe the flow through the reactor. This model is popularly known as the convection-dispersion model, and characterizes mass transport in the axial direction in terms of an effective or apparent longitudinal

dispersivity that is superimposed on the plug flow velocity. The model also assumes that the fluid velocity and species concentrations are constant across the tube diameter. The magnitude of the dispersion is assumed to be independent of position within the column, so there are no stagnant regions and no by-passing or short-circuiting of fluid in the model reactor (Fogler, 1992).

The initial and boundary conditions for the experimental condition were given by:

Initial condition:

$$C_i(x,0) = 0 \quad (2)$$



The axial dispersion parameter is a term that accounts for mixing both by molecular diffusion processes and by turbulent eddies and vortices. These two types of phenomena were characterized by a single parameter, which is obtained by adjusting the parameter to fit the experimental data. The response of the axial dispersion model to changes in the inlet concentration can be described by the following partial differential equation (Fogler, 1992):

$$\frac{\partial C_i}{\partial t} = D_L \frac{\partial^2 C_i}{\partial x^2} - u \frac{\partial C_i}{\partial x} \quad (1)$$

In Equation (1),  $C_i$  is the concentration of species  $i$ ,  $D_L$  represents the dispersion coefficient,  $u$  is the superficial velocity through the column and  $x$  is the distance from the inlet of the column.

Boundary conditions:

$$\begin{aligned} C_i(0,t) &= 1 \\ \frac{dC_i(L,t)}{dx} &= 0 \end{aligned} \quad (3)$$

In the above equation,  $L$  is the length of the column. Solution of Equation (1) with the initial and boundary conditions given in Equations (2)-(3) is given by:

$$F(t) = \frac{1}{2} \left[ 1 - \operatorname{erf} \left\{ \frac{1}{2} \sqrt{\frac{uL}{D_L}} \left( \frac{1 - \frac{t}{t^*}}{\sqrt{\frac{t}{t^*}}} \right) \right\} \right] \quad (4)$$

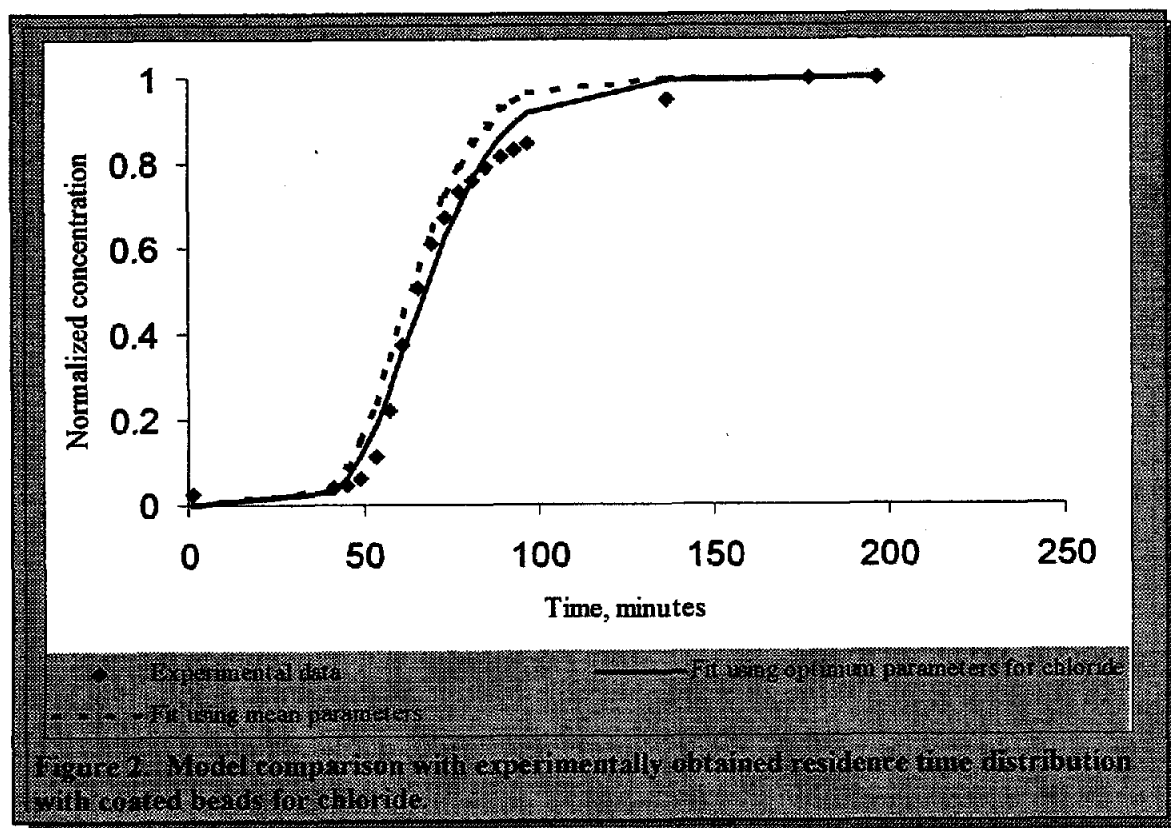
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where  $F(t)$  = concentration at column outlet normalized with respect to the inlet concentration,

and  $\frac{uL}{D_L}$  = Peclet number (dimensionless),  
 $t^* = L/u$

values of the two parameters. The "best fit" estimates of the Peclet number and porosity for the ionic species are presented in Table 1.

The mean value of the dispersion coefficient and porosity were  $0.22 \text{ cm}^2/\text{min}$  ( $\pm 0.074 \text{ cm}^2/\text{min}$ ) and



The superficial velocity through the column,  $u$ , was estimated using the equation:

$$u = \frac{Q}{A \cdot \Phi} \quad (5)$$

In the above equation,  $Q$  is the volumetric flow rate,  $A$  is the cross-sectional area of the column, and  $\Phi$  is the bed porosity. Two adjustable parameters, the Peclet number,  $uL/D_L$ , and the porosity,  $\Phi$ , were used to fit the model to the experimental data. Since the analytical solution (Equation 4) was available, a simple spreadsheet utilizing the Solver routine in Microsoft Excel 5.0 was used to determine the "best fit" values of the two parameters. In this case, the sum of squared errors between the model predicted responses and experimental data was used as the objective function. The Solver routine was used to minimize this objective function by adjusting the

Table 1. "Best fit" Peclet number and porosity estimates for various ionic species

| Ionic species      | Peclet number | Bed porosity |
|--------------------|---------------|--------------|
| Acetate            | 36.86         | 0.6501       |
| Chloride           | 29.06         | 0.6064       |
| Nitrite            | 36.69         | 0.6076       |
| Nitrate            | 23.91         | 0.6090       |
| Phosphate          | 49.13         | 0.5690       |
| Selenite           | 26.99         | 0.4360       |
| Mean               | 33.77         | 0.5797       |
| Standard deviation | 9.1557        | 0.0749       |

0.57 ( $\pm 0.075$ ). The model comparison with the experimental data for a representative ionic species

chloride is presented in Figure 2. Both the "best fit" parameters for chloride as well as the mean values of the parameters fit the experimental data well. The fits of the other ionic species are equally good.

The mass transfer coefficient was then estimated for various ionic species by fitting the model to the experimental data obtained using the uncoated beads. In this case, a term was added to Equation (1) to account for the transport of various species into the beads:

$$\frac{\partial C_i}{\partial t} = D_L \frac{\partial^2 C_i}{\partial x^2} - u \frac{\partial C_i}{\partial x} - k(C_i - C_{p_i}) \quad (6)$$

$$\frac{\partial C_{p_i}}{\partial t} = k(C_i - C_{p_i}) \quad (7)$$

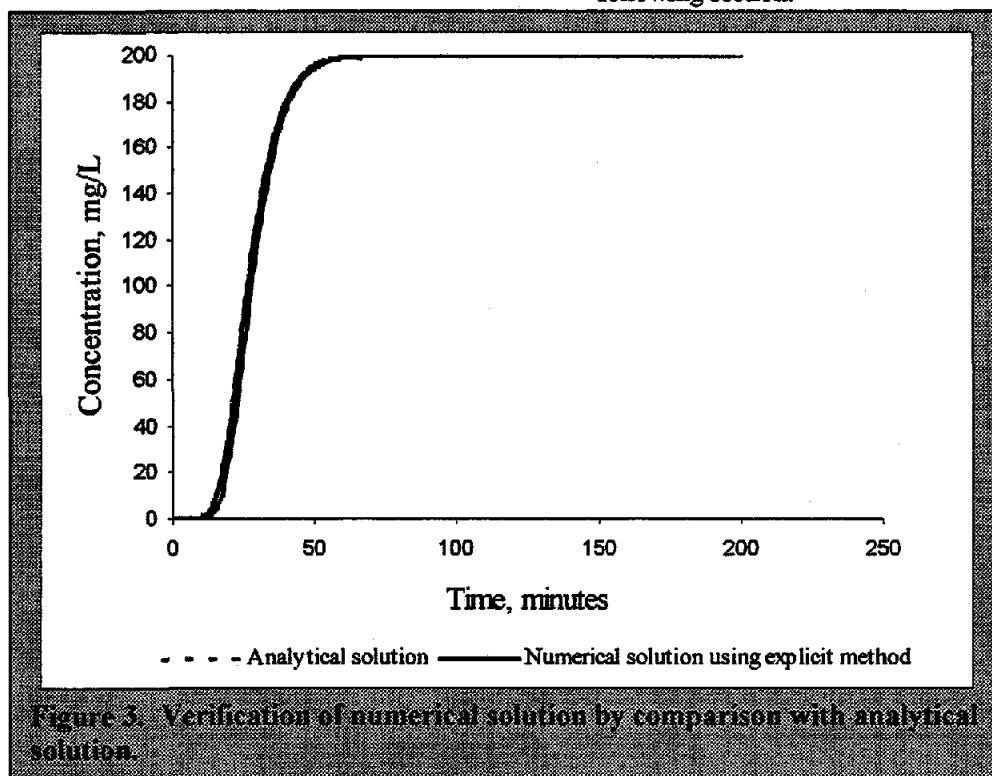
where  $C_{p_i}$  = concentration of species  $i$  inside the beads.

The boundary conditions were the same as previously described in Equations (2)-(3). The parameter  $k$  is the mass transfer coefficient of the ionic species into the beads. The mass transfer into the beads was assumed to be proportional to the concentration difference between the bulk liquid

phase and that inside the beads for each of the individual species. A numerical solution procedure using an explicit method was used to solve Equations (6)-(7). The solution was verified by comparing the predictions to the analytical solution of Equation (4) for the case when no mass transfer occurred (Figure 3). As can be seen from Figure 3, there is excellent agreement between the numerical solution and the analytical solution.

Once the solution procedure was verified, the mass transfer coefficient for each species was determined by minimizing the sum of squared errors between the model predicted values and experimental data. In this instance, a numerical optimization procedure using the golden search method was used.

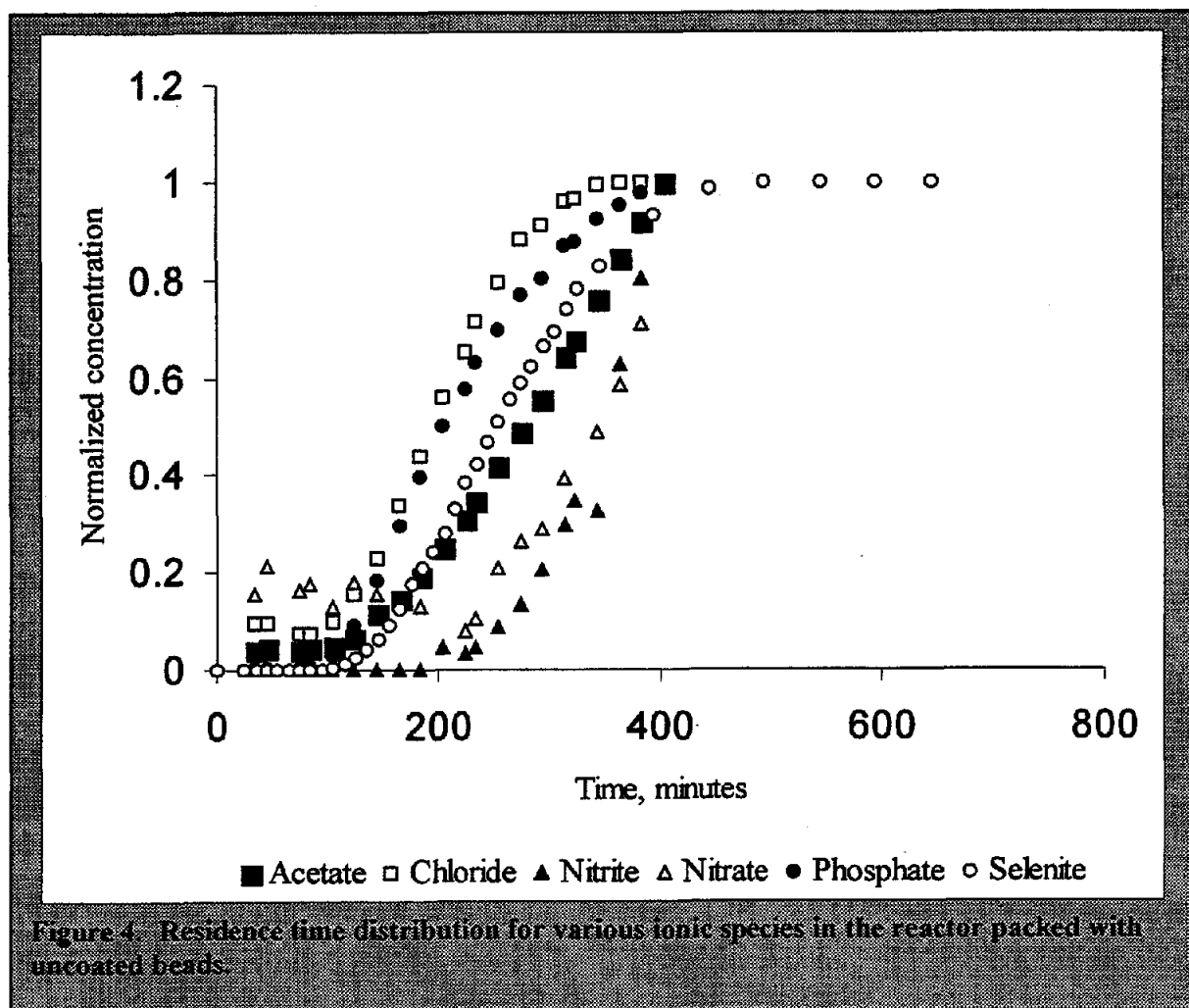
The "best fit" values of the mass transfer coefficients were then compared for the duplicates and various ionic species using SAS<sup>TM</sup> (PROC ANOVA). The null hypothesis tested was that the mass transfer coefficient for all the ionic species was the same. This hypothesis was tested against the alternative hypothesis that not all the ionic species had the same mass transfer coefficient. A p-value of less than 0.01 indicated that a single value of the mass transfer coefficient represented by the mean of the values of various species could not be used in the model. The reasons for this disparity in values for various species and its implications are discussed in the following section.



## DISCUSSION

The residence time distributions of the various ionic species in the case of uncoated beads are shown in Figure 4.

species in the column effluent until all of active sites are occupied. Further, these species interact with the activated carbon at different rates, thus explaining the differences in residence time distributions among



As can be seen from this figure, acetate, nitrate, selenite and nitrite do not elute from the column at the same rate as chloride and phosphate. The apparent lag in the residence time distribution of these species can be explained by the possible interaction of these species with the activated carbon in the exterior of the beads. This interaction could be a chemical interaction or physical sorption onto the surface of the activated carbon, and was not determined in this study. Such an interaction of species onto the surface of these beads has been implicated in prior studies (Ross, 1997). If acetate, nitrate, selenite and nitrite occupy the active sites of the beads, then there would be slow elution of these

them. Hence, for further analysis and estimation of the mass transfer coefficient, chloride and phosphate were considered.

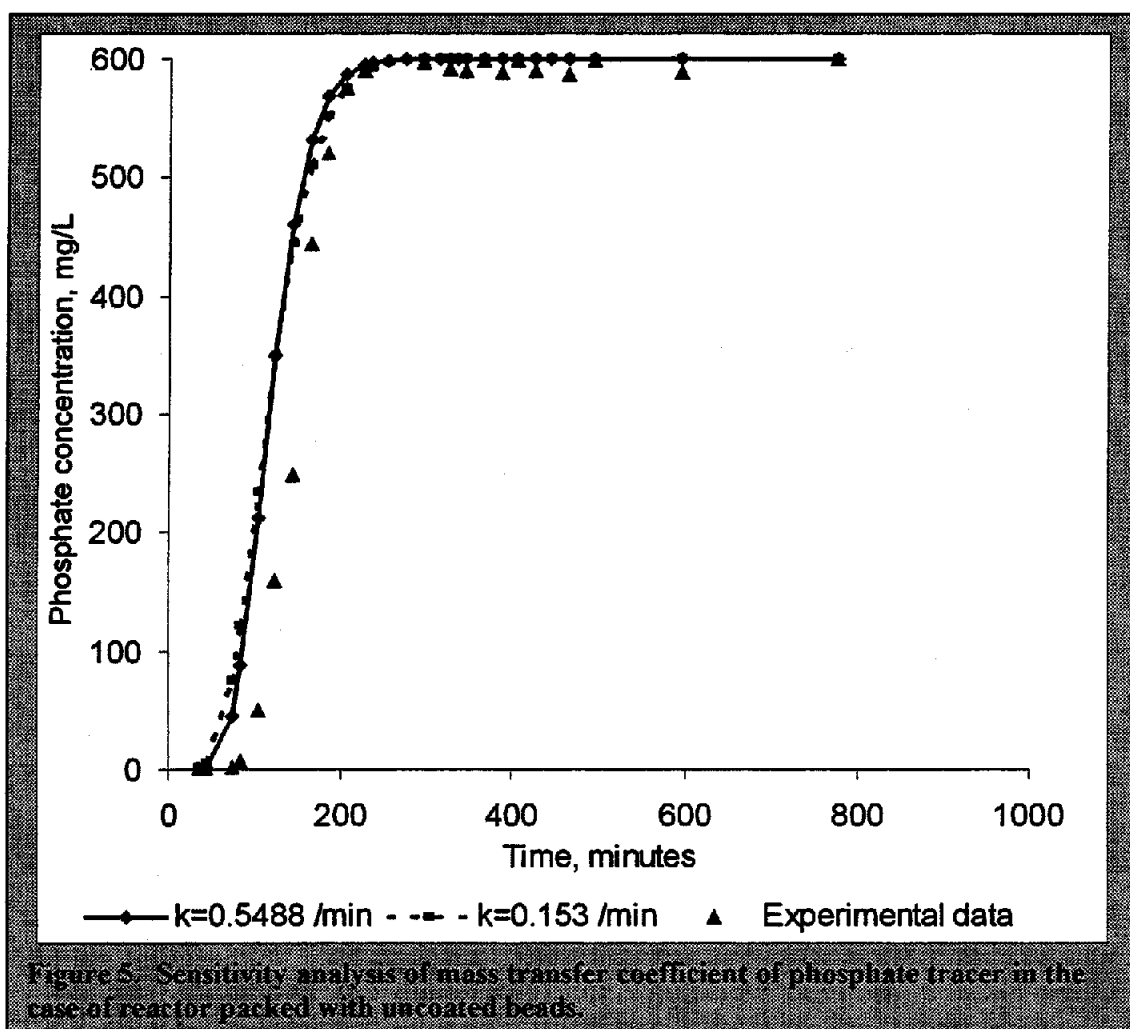
The "best fit" values for the mass transfer coefficients for chloride and phosphate were 0.15305 /min ( $\pm 0.0007$  /min) and 0.5512 /min ( $\pm 0.0033$  /min). The ANOVA procedure was used to determine if the two species chloride and phosphate with seemingly identical residence time distributions had the "same" mass transfer coefficient. PROC ANOVA was used again with the Duncan's multiple range test to determine whether the two species had statistically identical mass transfer coefficients. The results of this test indicated that the two species had

statistically different mass transfer coefficients. Next, a sensitivity analysis was performed to determine if there was any practical significance of using the mass transfer coefficient of one species for the other. The mass transfer coefficient for chloride was used in the prediction of the phosphate residence time distribution, and vice versa.

probably a reasonable estimate for application in the model.

## CONCLUSIONS

In this paper, we have presented a general description of the classes of mathematical models, procedures to obtain estimates of the model



The results of this analysis are presented in Figure 5 for phosphate. In this figure, the model predictions by using the mass transfer coefficient for chloride as well as the "best fit" value for phosphate are compared against the experimental data for phosphate. As can be seen from this figure, the use of the mass transfer coefficient of one species for the other does not significantly affect the results of the predictions. Hence, the mass transfer coefficient, which is represented by the average of the parameters estimated for these two species is

parameters and methods of validating the model parameters. Later, we have presented a case study in which we have obtained the parameters describing the transport of various ionic species through a columnar reactor. The use of empirical as well as phenomenological approach is demonstrated. The empirical model yields good regression coefficients, indicating excellent fit with the experimental data. However, its predictions cannot be relied on to obtain physically realistic predictions. Its predictions in the first few minutes result in negative

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concentrations of the ionic species, which is physically unrealistic in this situation.

An analytical solution was used to obtain the dispersion coefficient and porosity using a phenomenological model. The dispersion coefficient and porosity were estimated from experimental data using coated beads. The standard deviations of these parameter estimates were less than the parameter values and the fits of the model predictions to the experimental data were reasonable. The mass transfer coefficient was then obtained using experimental data for the same ionic species, but in this case, uncoated beads were used. The residence time distributions in this case were not the same for the six species studied. Acetate, nitrate and nitrite were found to elute slowly compared to chloride and phosphate. The reason for this difference can be attributed to the adsorption of these species onto the activated carbon of the beads. For the chloride and phosphate, the mass transfer coefficients were statistically different, but not practically different. The phenomenological approach can be used to suitably design a remediation system for selenium using Bio-Sep™ beads. By changing the operating conditions, such as the flow rate, it is possible to investigate the effects on the residence time distributions without actually carrying out any expensive and time-consuming experimentation.

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