Unbiased Identification of Nonlinear Sorption Characteristics by Soil Column Breakthrough Experiments *

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28th October 1997

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Abstract

Accurate identification of interactions of reactive solutes with porous media constituents is necessary for reliable risk assessment studies and the development of efficient sanitation strategies. Standard parameter estimation procedures bear a number of unsolved problems with respect to uniqueness and identifiability. This paper presents a new approach for the identification of nonlinear interaction parameters of column outflow experiments. The procedure requires no a priori assumptions on the shape of the underlying interaction process functions. Employing experimental data sets on cadmium and anthracene breakthrough as case studies, possible applications of the new approach will be shown and its features will be discussed. Error analysis based on singular value decomposition of the sensitivity matrix quantifies the identification error. Identification procedures without a priori shape information are superior to fixed parametrizations in diagnostic investigations, especially in cases without reliable a priori knowledge on the sorptive interactions.

Keywords. reactive flow in porous media, inverse problems for pde, parameter identification, multi-level optimization
Mathematics Subject Classification. 86A22, 86-08, 35R30, 35K57, 34H05, 35K65

*submitted to Water Resources Research
1 Introduction

Column outflow experiments play a prominent role in the understanding and identification of transport and reaction processes of contaminants in porous media [Dunnivant et al., 1992, De Smedt and Wierenga, 1984, Biggar and Nielsen, 1962, Selim et al., 1977, Brusseau and Rao, 1991, Schweich and Sardin, 1981, Jr. and Miller, 1988, Enfield et al., 1989, Totsche et al., 1997]. In particular, soil column experiments are used to identify partitioning coefficients, ion-exchange or sorption isotherms under natural flow conditions. To obtain reaction parameters from miscible displacement experiments, the column effluent concentration history, i.e. the breakthrough curve, is analyzed employing either graphical or mathematical procedures [Glueckauf, 1949, Schweich et al., 1983, Parker and van Genuchten, 1984, Rainwater et al., 1987, Kool et al., 1989, Bürgisser et al., 1993, van Veldhuizen et al., 1995]. Provided a uniform and steady state water flow regime, the shape of the measured breakthrough curve is determined by the column dispersivity and interactions (e.g. ion-exchange, adsorption, surface complexation, partitioning) of the solute with (usually immobile) components of the porous media. Mathematical analysis of the breakthrough curve is done by numerical inversion of an adequate transport model. Most frequently, the advection-dispersion equation (ADE) is used to describe the transport phenomena. To account for reactive interactions, the ADE is explicitly coupled with one of a number of possible interaction equations, e.g. simple partitioning, Freundlich-type, Langmuir-type or the BET-type isotherms [Kinniburgh, 1986]. The decision for a specific interaction equation is thereby more or less arbitrary: It depends on either the suggested interaction process, e.g. for hydrophobic contaminants most frequently a partition model is used, on the expertise of the experimenter or simply on the available models for parameter estimation. The resulting reactive transport model is then combined with a nonlinear output least-square curve fitting procedure. This approach can produce misleading results, if the a-priori assumption on the shape does not comply with the actual, underlying interaction process. Such a method will provide adequate results as long as one is exclusively interested in finding the best-fit parameter values for a given and known sorption process. If the task is to identify and discriminate between competing processes and properties controlling the interaction this approach might result in a complete misinterpretation of the underlying sorption process: The a-priori assumptions on the shape embedded in the algorithm forces the OLS procedure to yield the respective sorption isotherm. Any other outcome of the fitting procedure is impossible. E.g., breakthrough curves, which are controlled by linear or convex \( (ds^2/dc^2 > 0) \) nonlinear sorption reactions are forced to follow the Langmuir isotherm, which essentially exhibits concave shape \( (ds^2/dc^2 < 0) \) due to saturation type sorption. In this case the fitting algorithm either fails to meet the fitting criteria, or - if the algorithm allows the simultaneous fitting of multiple coefficients - another parameter, e.g. the column dispersivity, compen-
sates the erroneous behavior of the identification procedure. Most frequently, a possible misidentification is not recognized. The coefficients which are yield by the fitting procedure are often accepted, as still plausible parameter values usually span more than one order of magnitude. In this paper, we will introduce a new method for the identification of nonlinear and also rate limited sorption characteristics from column outflow experiments. A similar approach has been shown by Chavent et al. [1994], who estimated capillary pressures from centrifuge experiments. The proposed procedure is free of any assumptions on the shape of the underlying sorption isotherm, eg no a-priori information on linearity or curvature is required. However, if a priori information can be provided (eg monotonicity or concavity of the isotherm), the additional information can be taken into consideration as restrictions. This leads to further acceleration and stabilization of the identification procedure. Generally, the proposed approach circumvents the disadvantages of classical curve-fitting algorithms by allowing any kind of nonlinear sorption characteristics, thus being suitable for diagnostic investigations of column outflow experiments. The present study considers single-solute miscible displacement experiments with spontaneous nonlinear sorption characteristics, but can easily be adapted to rate limited sorption interactions, too.

2 Model Statement

For the following reasoning we consider one-dimensional reactive solute transport. These conditions are typically met for laboratory soil column experiments with Peclet numbers ranging from $\frac{1}{10}$ to 100 and with steady-state water flow conditions, but these assumptions are not necessary for the following.

Solute transport can then be described adequately by the following nonlinear partial differential equation, which describes the advective-dispersive transport for $x \in (0, \hat{t})$ and $t \in (0, \hat{t})$:

$$\partial_t (\Theta c)(x, t) + \rho \partial_t s(x, t) - \partial_x (D \partial_x c - qc)(x, t) = 0$$

$$c(x, 0) = c_{\text{ini}}(x)$$

$$-(D \partial_x c - qc)(0, t) = qc_0(t)$$

$$\partial_x c(\hat{t}, t) = 0$$

Here, $\hat{t}$ \, [L] denotes the column length, $\hat{t}$ \, [T] the time of complete breakthrough of the solute, $c(x, t)$ \, [ML$^{-3}$] the mass concentration of the solute related to the water filled part of the porous medium, $c_{\text{ini}}$ \, [ML$^{-3}$] initial mass concentration of the solute, $s(x, t)$ \, [MM$^{-1}$] mass concentration of solute sorbed to the immobile phase, $\varphi(c)$ \, [MM$^{-1}$] c-sorption-characteristic (i.e. the sorption isotherm), $\Theta(x, t)$ \, [1] volumetric water content, $\rho(x)$ \, [ML$^{-3}$] mass fraction of sorption site, $D(x, t)$ \, [LT$^{-2}$] diffusion-dispersion coefficient, $q(x, t)$ \, [LT$^{-1}$] Darcy flow velocity.
$c_0(t) [ML^{-3}]$ inflow concentration at inlet $x = 0$, and $x [L]$ and $t [T]$ the variables of space and time, respectively.

The reactive interaction of the solute is described either by sorption of the solute to the surface of the porous media or by partitioning between the mobile and the immobile phase. In the equilibrium case, the functional dependency is given by

$$s = \varphi(c)$$

or as additional nonlinear ODE in the non-equilibrium case:

$$\partial_t s = f(c, s) = k(\varphi(c) - s),$$

where we have applied a commonly used heuristic approach for the rate function $f$. This model may also be understood as a building stone for more complex models, eg for carrier-influenced reactive transport ([Knabner et al., 1996], [Totsche et al., 1996]). The necessary observation is given by outflow concentration measurements with $g(t) [ML^{-3}]$ at $x = \bar{l}$:

$$g(t) = c(l, t).$$

### 3 Numerical Identification

The numerical identification procedure is based on the Output Least Squares Method (OLS) which provides the standard approach to the solution of the identification problem: The OLS functional

$$J(p) = \sum_{k,j=1}^{N} \alpha_{kj}(g(t_k) - g^*_k)(g(t_j) - g^*_j)$$

with weighting factors $\alpha_{kj}$ (eg coefficients of the inverse covariance matrix) and $N$ measurements $g^*_k$ at times $t_k$ has to be minimized by an optimal parameter vector $p^* = (p^*_1, \ldots, p^*_s)$.

In the following we will identify sorption characteristics. In a preliminary step the dispersion coefficient has to be determined independently, which can be done by a similar approach.

In principle, our approach could be used to identify both sorption and dispersivity by one outflow experiment. However, this would lead to well-known uniqueness problems [Kool et al., 1989, Roy, 1992, DuChateau, 1995a,b]: Generally, inverse modeling does not lead to unique identifications, as measurement errors distort the identification procedure. However, in the absence of measurement errors, the unknown coefficients are supposed to be uniquely determined by measurements. As a rule of thumb, this is considered to hold true, as long as the number of unknown coefficient functions equals the number of additional measurements (over-specification), eg sorption isotherm as coefficient function...
and breakthrough curve as additional measurement. (The validity of this rule of thumb has been proved for several applications \cite{lgler1997, duChateau1995a}.) If the number of unknowns exceeds the level of overspecification, uniqueness can be lost even in the absence of measurement errors: The OLS functional can be minimized by an infinite amount of (completely) different solutions, which all are in accordance with the (insufficient) measurements.

### 3.1 Parametrization

The choice of parametrization \( \varphi(c) = \varphi_p(c) = \varphi_{p_1, \ldots, p_r}(c) \) of the \( c-s \)-characteristic is crucial for the performance of the identification algorithm and the relevance of the identification results.

We abandon the usage of a-priori shape information (like Freundlich or Langmuir approach) for parametrization, as it is not obvious that the initially unknown \( c-s \)-characteristic can be represented appropriately by any specific formula. We choose free-form parametrizations which guarantee that every parameter has only local effects on the shape of the characteristic: piecewise linear functions with \( \varphi(c_i) = p_i \) for given discretization points \( c_i > 0 \), parameters \( p_i \geq 0 \) and additionally \( \varphi(0) = 0 \). (In general we consider piecewise polynomial functions.) In the non-equilibrium case the sorption rate \( k \) is augmented as additional parameter \( p_{r+1} \).

Furthermore our parametrization must not depend intrinsically on the physical units that represent the concentration values \( c \) and \( s \). If we consider an isotherm \( \varphi_p(c) \) and a rescaling \( c \mapsto c/\bar{c} \), then there has to be a parameter vector \( \bar{p} \) and an isotherm \( \bar{\varphi} \) of the same parametrization type such that \( \varphi_p(c)/\bar{c} = \bar{\varphi}_{\bar{p}}(c/\bar{c}) \). This condition is satisfied for piecewise linear functions and the rescaling of the isotherm is easily obtained by \( c_i \mapsto c_i/\bar{c} \) and \( p_i \mapsto p_i/\bar{c} \). (It is also possible to rescale Freundlich and Langmuir isotherms appropriately. In general, this rescaling involves more complicated nonlinear transformations.)

We note that the shape of the piecewise linear characteristic which represents the result of the identification procedure can be taken to fit the desired function (Freundlich, Langmuir, etc.) a-posteriori.

### 3.2 Multi-Level Identification

The simulation of a breakthrough curve for a given sorption characteristic is denoted as direct problem. The identification of the sorption characteristic for a given breakthrough curve inverts the direct problem and is called solution of the inverse problem. This inverse problem is ill-posed: For perturbed measurements there may not exist any sorption characteristic which can reproduce exactly the measured breakthrough curve. Low sensitivity of the breakthrough curve with respect to the sorption characteristic can lead to arbitrarily high identification errors for hounded and even small measurement errors.
The ill-posedness can be treated by an OLS ansatz and by regularizing the inverse problem. In our case regularization is obtained by choosing a finite dimensional parameter space. Low regularization means a high number \( r \) of degrees of freedom, and vice versa. A low number \( r \) leads to a stable identification procedure with the disadvantage of producing only a rough guess of the sorption characteristic. In the case of growing numbers of degrees of freedom \( r \) we observe semi-convergence: As the parameter space is able to reproduce the shape of a sorption characteristic with higher precision, the identification result gets better. If the number of degrees of freedom gets too high and consequently the amount of regularization drops beyond a certain level in relation to the error (by measurement, modeling, discretization, etc.) level, the identified characteristic gets worse. High frequency errors appear and the identified coefficient again moves away from the actual sorption characteristic.

A multi-level ansatz coupled with sensitivity analysis provides an adequate number of degrees of freedom \( r \) and avoids typical problems of optimization procedures in the case of weak sensitivity and high numbers of degrees of freedom (slow convergence, the process gets trapped in a local minimum). We illustrate this by two examples.

### 3.2.1 Example: Breakthrough of Cadmium

The heavy metal cadmium was filtrated through an initially cadmium-free \( (c|_{t=0} = 0) \) soil column (Table 2 and [Dunnivant et al., 1992]) packed homogeneously with aquifer material and saturated with DOM. The inflow concentration \( c_0(t) = c_t \) was chosen to be constant.

The identification procedure starts with 1 degree of freedom, i.e. a linear characteristic \( \varphi^1 \) with \( \varphi^1(c_0) = p_1 \). The characteristic which minimizes the OLS functional is depicted as solid line in Figure 1 (left). Figure 1 (right) shows the measured breakthrough curve (btc) as dots \( g_k^* \) and the simulated btc as solid line \( g(t) \). (Time is scaled to pore volumes \( pv \).) The btc was measured completely, i.e. the measured values \( g_k^* \) finally reach the asymptotic value \( c_0 \). Identification with a linear characteristic provides already good results.

In the next step the number of degrees of freedom is incremented to 2. We now have to find the parameters \( p_1 = \varphi^2(c_0/2) \) and \( p_2 = \varphi^2(c_0) \). We take the information which was obtained in the previous optimization procedure as start value for the next optimization: The linear characteristic \( \varphi^1 \) is interpolated for \( c_0/2 \) in order to obtain \( p_1 = \varphi^1(c_0/2) \) and for \( c_0 \) in order to obtain \( p_2 = \varphi^1(c_0) \). Running the optimization with these start values we obtain a better fit of the btc. The corresponding characteristic \( \varphi^2 \) is composed of two linear functions.

The whole interpolating procedure is now performed again for three degrees of freedom at \( c_0/2, 3c_0/4 \) and \( c_0 \): \( p_1 = \varphi^2(c_0/2), p_2 = \varphi^2(3c_0/4) \) and \( p_3 = \varphi^2(c_0) \).

Another interpolation and optimization step for \( c_0/4, c_0/2, 3c_0/4 \) and \( c_0 \) yields a significant improvement over the first result (Figure 2).
The procedure is continued until we reach 8 degrees of freedom \( (c_0/8, c_0/4, 3c_0/8, c_0/2, 5c_0/8, 3c_0/4, 7c_0/8, c_0) \). If we compare the results to those for 4 degrees of freedom, we realize that only oscillations have been added. The overall quality of the fit has not improved (Figure 3).

As we observe that the isotherm is given by an almost linear function with a slightly convex deformation, the isotherm can be considered to be of Freundlich-type with \( p > 1 \). An a-posteriori fit with Freundlich parametrization to the result obtained in step 4 provides \( \varphi_{\text{Freundlich}}(c) = 65.74 \cdot c^{1.12} \). This isotherm is displayed in Figure 4 by a solid line together with dots which represent the result from identification step number 4 \( (\varphi^4) \).

Numerical experiments show that the multi-level approach prevents the optimization from getting trapped in local minima and essentially accelerates the identification process.

3.2.2 Example: Breakthrough of Anthracene

The chemical anthracene was filtrated through an initially clean \( (c|_{t=0} = 0) \) soil column packed homogeneously with spodic material. The inflow concentration \( c_0(t) = c_0 \) was chosen to be constant (Table 2 and [Totsche et al., 1997]).

The BTC was not measured completely, i.e. the measured values \( g_x^t \) do not exceed \( 0.5c_0 \). The identification with a linear characteristic provides poor results. In the next identification step we choose two degrees of freedom in \( c_0/4 \) and \( c_0 \). Successive refinements finally lead to eight degrees of freedom in \( c_0/16, c_0/8, 3c_0/16, 2c_0/8, 5c_0/16 3c_0/8, 7c_0/16, c_0 \).

Comparison of the results from steps 1, 2 to the result from step 8 shows that a significant improvement is obtained (Figure 5).

The measured values do not exceed \( 0.5c_0 \). However, inside the soil column higher \( c \)-values can be found, and \( \varphi(c) \) influences the behavior of the concentration profile for \( c > 0.5c_0 \), too. In the absence of measurement errors the breakthrough curve would provide enough information to determine \( \varphi(c) \) for all \( c \)-values which have been reached for any \( x \) and \( t \) in the soil column (see [Igler and Knabner, 1997, DuChateau, 1995a]). As information about \( \varphi(c) \) beyond the level \( 0.5c_0 \) is only given indirectly, the sensitivity for \( c > 0.5c_0 \) is very low. If we take the measurement errors into account, we should choose the number of degrees of freedom in the region \( c > 0.5c_0 \) to be very low, too. Considering our choice of parametrization — piecewise linear — a straight line between the \( c \)-value that is next to \( 0.5c_0 \) and the value at \( c_0 \) yields an acceptable compromise between stability and accuracy.

Despite these limitations the identification is able to reveal clearly, that the sorption isotherm is almost linear in the interval \([0, 0.5c_0]\) and changes its slope significantly at \( 0.5c_0 \). An a-posteriori fit with Freundlich parametrization is possible, but is discouraged by these results.
3.3 Error Analysis

The identification is qualified with the help of a singular value decomposition (see e.g. [Golub and van Loan, 1996]) of the sensitivity matrix. First order expansion of $0 = \delta F$ at the minimum gives

$$\frac{\partial g}{\partial p} \delta p \approx \delta g,$$

\[ (9) \]

i.e. deviations in the measurement error $\delta g$ are coupled with deviations in the identification error $\delta p$ by the sensitivity matrix $\frac{\partial g}{\partial p}$. A singular value decomposition of the sensitivity matrix yields a singular system $\{v_n, u_n; \sigma_n\}$ with the following properties: \{\sigma_i\} are the square roots of the eigenvalues of the symmetric, positive definite matrix $\frac{\partial g}{\partial p}^T \frac{\partial g}{\partial p}$. The set of vectors $\{u_j\}$ and $\{v_j\}$ form orthonormal bases of range($\frac{\partial g}{\partial p}$) and range($\frac{\partial g}{\partial p}^T$), such that the identification-measurement-error relations reads

$$\delta p \approx \sum_j \sigma_j^{-1} \langle \delta g, u_j \rangle v_j.$$  

We thus obtain two characteristic numbers:

- maximum error amplification: $\sigma := \max_j \sigma_j^{-1}$,
- (generalized) condition number: $\kappa := \max_{j,k} \frac{\sigma_j}{\sigma_k}$.

The numbers $\sigma$ and $\kappa$ can serve as boundaries for confidence intervals or as stopping criterion for a multi-level process.

The singular values for the first example (cadmium) are displayed in Figure 6. We start with a total error amplification of about 10 and finally reach about 40. This corresponds to the observation that only oscillations are added in the last identification steps. The condition number increases from about 2 to approximately 3. That means that the error amplification is increased, whereas the identification stays almost equally sensitive to all parameters.

3.4 Implementation Details

We used fast optimization procedures (for example the SQP method described in [Schittkowski, 1988]) which involve the computation of the functional value and its derivative. As there is no closed-form solution available for the above mentioned mathematical model, we have to solve the nonlinear PDE / ODE numerically: Euler steps in time and Finite Elements in space as in [Knabner, 1992]. The easiest way to compute the gradient is too costly and numerically unstable: finite differences as approximations for the partial derivatives $\partial F/\partial p_i$. We obtain the gradient by means of an adjoint problem which needs about the same amount of CPU time as the solution of the PDE / ODE. The optimization is stabilized by constraints, e.g. monotonicity of the characteristic ($p_{i+1} \geq p_i$). (Details can be found in [Igler and Knabner, 1997].)
4 Conclusion

We present a new numerical tool for the identification of nonlinear sorption characteristics by soil column breakthrough experiments. The numerical identification procedure is based on the classical OLS method and mainly differs from standard approaches in the choice of the parameterization. We focus on the identification of a functional dependence and consequently abandon the assumption of a-priori shape information. The nonlinear characteristic is parametrized piecewise linearly and identified in an adaptive multi-level procedure, which yields successively more detailed information. The identification error is quantified by a singular value decomposition of the sensitivity matrix.

This has several advantages over fixed parametrizations like Freundlich or Langmuir: Characteristics of arbitrary shape are regarded up to an adjustable accuracy, which can be adapted to the measurement error. The resulting piecewise linear characteristic transforms easily under scale changes. If a certain characteristic type (like Freundlich or Langmuir) can be recognized after termination of the identification procedure, it is possible to obtain the corresponding parameters in a fast a posteriori fit.

Our implementation of the OLS method applies the solution of a discrete adjoint problem for the computation of the gradient of the OLS functional. This accelerates essentially the identification procedure, as the computation of the gradient is fast in comparison to eg finite difference approximation, and the higher accuracy of the approximated gradient leads to fewer optimization steps.

References


<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \hat{t} )</td>
<td>[L]</td>
<td>length of the soil column</td>
</tr>
<tr>
<td>( \bar{t} )</td>
<td>[T]</td>
<td>termination time of the experiment</td>
</tr>
<tr>
<td>( c(x, t) )</td>
<td>[ML⁻³]</td>
<td>dissolved concentration of the chemical</td>
</tr>
<tr>
<td>( c_{i0}(x) )</td>
<td>[ML⁻³]</td>
<td>initial dissolved concentration of the chemical</td>
</tr>
<tr>
<td>( s(x, t) )</td>
<td>[MM⁻¹]</td>
<td>sorbed concentration of the chemical</td>
</tr>
<tr>
<td>( \varphi(c) )</td>
<td>[MM⁻¹]</td>
<td>c-s-sorption-characteristic = isotherm</td>
</tr>
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<td>( \Theta(x, t) )</td>
<td>[1]</td>
<td>volumetric water content</td>
</tr>
<tr>
<td>( \rho(x, t) )</td>
<td>[ML⁻³]</td>
<td>mass fraction of sorption site</td>
</tr>
<tr>
<td>( D(x, t) )</td>
<td>[LT⁻²]</td>
<td>diffusion-dispersion coefficient</td>
</tr>
<tr>
<td>( q(x, t) )</td>
<td>[LT⁻¹]</td>
<td>Darcy flow velocity</td>
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<tr>
<td>( c_0(t) )</td>
<td>[ML⁻³]</td>
<td>inflow concentration at inlet ( x = 0 )</td>
</tr>
<tr>
<td>( g(t) )</td>
<td>[ML⁻³]</td>
<td>outflow concentration at outlet ( x = \hat{t} )</td>
</tr>
<tr>
<td>( g^* )</td>
<td>[ML⁻³]</td>
<td>vector of measured outflow concentrations</td>
</tr>
<tr>
<td>( p, p^* )</td>
<td>[MM⁻¹]</td>
<td>vector of identification parameters</td>
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Table 1: Notation
### Table 2: Experimental Conditions

<table>
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<tr>
<th>Parameter</th>
<th>Anthracene</th>
<th>Cadmium</th>
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<tr>
<td>$l$ [cm]</td>
<td>7.26</td>
<td>7.95</td>
</tr>
<tr>
<td>diameter $d$ [cm]</td>
<td>9.4</td>
<td>1</td>
</tr>
<tr>
<td>$\Theta$ [1]</td>
<td>0.23</td>
<td>0.40</td>
</tr>
<tr>
<td>$\rho$ [$g \text{ cm}^{-3}$]</td>
<td>1.44</td>
<td>1.6</td>
</tr>
<tr>
<td>organic carbon content $\lambda$ [g cm$^{-1}$]</td>
<td>0.903</td>
<td>0.99958</td>
</tr>
<tr>
<td>dispersivity $\lambda$ [cm]</td>
<td>1.46</td>
<td>4.7</td>
</tr>
<tr>
<td>$q$ [cm s$^{-1}$]</td>
<td>2.9$\cdot$10$^{-4}$</td>
<td>1.06$\cdot$10$^{-2}$</td>
</tr>
<tr>
<td>$c_0$ [$g \text{ cm}^{-3}$]</td>
<td>27.4$\cdot$10$^{-9}$</td>
<td>0.25$\cdot$10$^{-6}$</td>
</tr>
</tbody>
</table>

### Table 3: Values of the Error Functional

<table>
<thead>
<tr>
<th>Number of Degrees of Freedom</th>
<th>Error Functional (in $r_o^2 \rho dw$)</th>
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<tbody>
<tr>
<td></td>
<td>Anthracene (8.70$\cdot$10$^{-14}$ g$^2$ cm$^{-3}$)</td>
</tr>
<tr>
<td>1</td>
<td>1.15$\cdot$10$^{-2}$</td>
</tr>
<tr>
<td>2</td>
<td>1.94$\cdot$10$^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>3.10$\cdot$10$^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>3.10$\cdot$10$^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>2.93$\cdot$10$^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>2.61$\cdot$10$^{-4}$</td>
</tr>
<tr>
<td>7</td>
<td>2.28$\cdot$10$^{-4}$</td>
</tr>
<tr>
<td>8</td>
<td>2.28$\cdot$10$^{-4}$</td>
</tr>
</tbody>
</table>
Figure 1: Cadmium. Identified Isotherm / Breakthrough Curve #1.

Figure 2: Cadmium. Identified Isotherm / Breakthrough Curve #4.
Figure 3: Cadmium. Identified Isotherm / Breakthrough Curve #8

Figure 4: Cadmium. A-posteriori Freundlich Fit.
Figure 5: Anthracene. Identified Isotherms / Breakthrough Curves # 1, 2 and 8.

Figure 6: Cadmium. Singular Value Decomposition.