# SOLUTION OF AN INVERSE MASS TRANSFER PROBLEM WITH THE PARTICLE COLLISION ALGORITHM

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***Abstract.*** *Inverse mass transfer problems involving biomolecules adsorption in resin beds have relevant applications in the food and pharmaceutical industry. The inverse problem approach has contributed in the estimation of physicochemical parameters for such applications which would be difficult to obtain if the standard experimental approach were used. The authors of the present work have used in previous works several different methods for the solution of both the direct and inverse mass transfer problems related to the liquid-solid adsorption phenomenon. In the present work we focus on the application of a recently developed method, the Particle Collision Algorithm, for the estimation of the adsorption isotherm coefficients.*

***Keywords****: Mass Transfer, Thomas Model, Inverse Problems, Particle Collision Algorithm.*

## 1. INTRODUCTION

It has been observed in recent years an increasing interest in inverse mass transfer problems (Tondeur et al., 2006, Ahmad and Guiochon, 2007), and such interest has mainly been driven by the food and pharmaceutical industries (Guiochon, 2002, Seidel-Morgenstein, 2004, Ahuja, 1991).

In many applications the inverse problem approach is more convenient (Forssén et al., 2006) or more accurate (Ahmad and Guiochon, 2007) than the standard approaches used to acquire a better understanding of the underlying mass transfer phenomena involved, or to estimate parameters in the mathematical models developed to describe such phenomena. As an example, the experimental determination of adsorption isotherms is an important step for the design of new methods in preparative chromatography (Fellinger et al., 2003). For such task the inverse problem of chromatography has provided the best estimates for the adsorption isotherm coefficients (Gritti and Guiochon, 2004).

In previous works we have formulated inverse mass transfer problems implicitly, as optimization problems, and have used deterministic, stochastic and hybrid methods for its solution (Câmara et al., 2007, Vasconcellos et al., 2003, Cuco et al., 2007, Lugon et al., 2007, Lage et al., 2006). Artificial Neural Networks have also been used (Lage et al., 2006a).

In the present work we are interested in the application of a recently developed stochastic method (Sacco et al., 2006), the Particle Collision Algorithm (PCA), for the estimation of adsorption isotherm coefficients. This novel stochastic method is inspired by the physics of the interaction of nuclear particles inside nuclear reactors.

In the iterative procedure implemented for the solution of the inverse problem it is required the solution of the direct problem. For that purpose we use the well known Thomas model (Thomas, 1944), which provides accurate results when the axial dispersion along the adsorption column is negligible (Folly et al., 2005).

## 2. MATHEMATICAL FORMULATION AND SOLUTION OF THE DIRECT PROBLEM

In Fig. 1 is shown a schematic representation of an adsorption column. It is composed by a fixed bed of adsorbent resins through which percolates a diluted solution of the adsorbate of interest. The adsorbate is transferred from the bulk of the solution to the vicinity of the resin particles, i.e. a mass transfer mechanism through the liquid, and then it diffuses to the interior of the particle pores, being then adsorbed by the solid matrix.

The mathematical model for the chromatography process is based on the mass balance for the two phases, one for the mobile phase that flows through the macroscale porous fixed resin bed, and the other for the resin particles involving the microscale porous solid matrix (Guiochon and Lin, 2003).

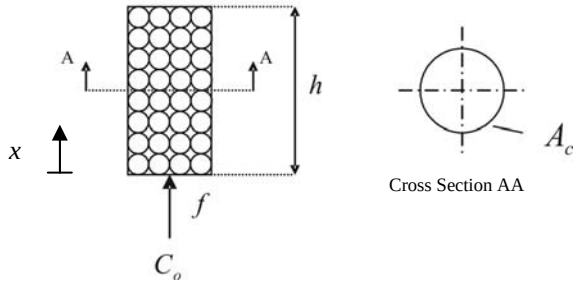



Figure 1 – Schematic representation of an adsorption column.

For the particular case in which the axial dispersion may be neglected and the adsorbate inflow is constant, i.e. $C_0 = constant$, the adsorption problem described previously has an analytical solution (Chase, 1984, Blanch and Clark, 1997, Rice and Do, 1994) which was first derived by Thomas (1944), and is therefore known as Thomas model. According to this model, the adsorbate concentration in the mobile phase at the exit of the adsorption column, i.e. at $x = h$, is given by

$$\frac{C}{C_0} = \frac{J(\eta/\sigma, \eta T)}{J(\eta/\sigma, \eta T) + [1 - J(\eta, \eta T/\sigma)]\exp[(1-(1/\sigma))(\eta - \eta T)]} \tag{1}$$

where

$$\sigma = 1 + C_o / k_d \tag{2}$$
$$\eta = q_m k_1 h A_c / fl \tag{3}$$
$$T = fl\, t\,(k_d + C_o)/ A_c q_m h \tag{4}$$

$k_d$ is the dissociation rate constant $(mg/ml)$, i.e. the ratio of the adsorption and desorption rate constants, $q_m$ is the maximum adsorbate concentration which the adsorbent may adsorb (maximum adsorption capacity) $(mg/ml)$, $k_1$ is the adsorption rate constant $(ml/mg \cdot \min)$, $h$ and $A_c$ are the length $(cm)$ and the cross section area $(cm^2)$ of the adsorption column, respectively, $t$ represents the time $(\min)$, $fl$ is the volumetric flow rate through the column $(ml/\min)$, and the function $J(a,b)$ is given by

$$J(a,b) = 1 - e^{-b}\int_0^a e^{-\xi} I_0(2\sqrt{b\xi})\, d\xi \tag{5}$$

where $I_0$ is the modified Bessel function of the first kind and of order zero.

The function $J(a,b)$ may be approximated by an asymptotic series whose two first terms are given by

$$J(a,b) \approx \frac{1}{2}\left[1 - erf\left(\sqrt{a} - \sqrt{b}\right)\right] + \frac{\exp\left[1 - \left(\sqrt{a} - \sqrt{b}\right)^2\right]}{2\pi^{\frac{1}{2}}\left[(ab)^{\frac{1}{4}} + b^{\frac{1}{2}}\right]} \tag{6}$$

From Eqs. (1-6) it is easily obtained the breakthrough curve, i.e. the adsorbate concentration at the exit of the column as a function of time.

## 3. INVERSE PROBLEM FORMULATION

After performing a sensitivity analysis (Folly et al., 2005, Lage et al., 2006a) it is possible to conclude that from the measured values of the adsorbate concentration at the exit of the adsorption column as a function of time, i.e.

$C_{\exp_i} = C_{\exp}(t_i),\ i = 1,2,\ldots,N$, where $N$ is the total number of experimental data, the parameter $q_m$ of the Langmuir adsorption isotherm

$$q = \frac{q_m C}{k_d + C} \tag{7}$$

may be the only adsorption isotherm parameter to be estimated accurately.

Therefore, in the present work we focus on the estimation of the unknown

$$\vec{Z} = \{q_m\} \tag{8}$$

The inverse problem is then formulated implicitly, as an optimization problem, in which we seek to minimize the squared residues cost function given by

$$Q(\vec{Z}) = \sum_{i=1}^{N} \left[ C_{calc_i}(\vec{Z}) - C_{\exp_i} \right]^2 = \vec{F}^T \vec{F} \tag{9}$$

where $C_{calc_i} = C_{calc}(t_i)$ represents the calculated values of the concentration obtained with the Thomas model, and the elements of the vector of residues $\vec{F}$ are written as

$$F_i = C_{calc_i}(\vec{Z}) - C_{\exp_i}, \qquad i = 1,2,\ldots,N \tag{10}$$

The concentrations considered in the present work are in fact the dimensionless concentrations given by $C/C_0$. Therefore, the cost function given by Eq. (9) is also dimensionless, as well as the elements of the vector of residues given by Eq. (10).

In order to minimize the cost function given by Eq. (9) we have used the Particle Collision Algorithm, which is described in the next section.

## 4. THE PARTICLE COLLISION ALGORITHM

The Particle Collision Algorithm (PCA) is loosely inspired in the physics of the interactions of neutrons in a nuclear reactor (Duderstadt and Hamilton, 1976), mainly scattering, being an incident particle scattered by a target nucleus, and absorption, being the incident particle absorbed by the target nucleus. Thus, a particle that hits a high-fitness "nucleus" would be absorbed, and would explore its neighborhood. On the other hand, a particle that hits a low-fitness region would be scattered to another region. This procedure permits the exploration of the search space and the exploitation of the most promising areas of the fitness landscape through successive scattering and absorption collision events.

The PCA resembles in its structure that of the Simulated Annealing (SA) (Kirkpatrick et al., 1983), i.e. first an initial configuration is chosen, and then a new configuration is obtained by performing a modification in the previous one. The quality of the two configurations is compared. A decision is then made on whether the new configuration is "acceptable". If that is the case, it becomes the old configuration for the next step of the iterative procedure. Otherwise, the algorithm proceeds with a new different change of the previous old configuration.

PCA may also be considered a Metropolis algorithm (Metropolis et al., 1953), i.e. a trial solution can be accepted with a certain probability even if the new configuration is worse than the old configuration. Such flexibility of the algorithm may avoid the convergence to local minima. In Fig. 2 is shown the pseudo-code for the PCA in its version for minimization problems.

The "stochastic perturbation" mentioned at the beginning of the loop shown in Fig. 2 consists in random variations in the values of each variable within their ranges prescribed a priori.

If the quality or fitness of the new configuration is better than the fitness of the old configuration, then the "particle" is "absorbed", and an exploitation of the neighborhood searching for an even better solution takes place. Function "Exploitation ( )" performs this local search, generating a small stochastic perturbation of the solution inside a loop. In PCA's standard version, it is a one-hundred-iteration loop.

The "small stochastic perturbation" is similar to the previous stochastic perturbation, but the new value for each variable is kept within a small vicinity of the original value.

Otherwise, if the quality of the new configuration is worse than the one for the old configuration the "particle" is "scattered". The scattering probability $\left(p_{scattering}\right)$ is inversely proportional to its quality. A low-fitness particle will

have a greater scattering probability. In a process similar to Monte Carlo's "Russian Roulette" (Duderstadt and Martin, 1979), the configuration is "scattered" (replaced by a random configuration) or, following Metropolis, survives, with its neighborhood being further explored ("else" branch of the function).

The solution of the inverse mass transfer problem under analysis consists on obtaining estimates for the unknown shown in Eq. (8) by minimizing the cost function given by Eq. (9) using the recently developed stochastic Particle Collision Algorithm (PCA) (Sacco et al., 2006), whose pseudo-code is shown in Fig. 2.

```
Generate an initial solution Old_Config
For n=0 to # of iterations
    Generate a stochastic pertubation of the solution
        If CostF(New_Config)<CostF(Old_Config)
            Old_Config := New_Config
            Exploitation ( )
        Else
            Scattering ( )
        End If
End For

Exploitation ( )
For n=0 to # of iterations
    Generate a small stochastic perturbation of solution
    If CostF(New_Config)<CostF(Old_Config)
        Old_Config := New_Config
    End If
End For
Return

Scattering ( )
p_scattering = 1 − Best_Fitness / Fitness(New_Config)
If p_scattering > random (0, 1)
    Old_Config := random solution
Else
    Exploitation ( )
End If
Return
```

Figure 2 – Pseudo-code for the Particle Collision Algorithm. Version for minimization problems.

## 5. RESULTS AND DISCUSSION

In Table 1 are presented the physico-chemical and process parameters related to real experiments performed by Chase (1984) with the substance lisozyme and Cibacron Blue Sepharose CL-6B.

Table 1: Physico-chemical and process parameters for Chase's experiments (1984) with lisozyme.

| Parameter | Units | Value |
|---|---|---|
| $h$ - column height | *cm* | 10.4 |
| $A_c$ - column cross section | $cm^2$ | 0.785 |
| $fl$ - volumetric flow rate | *ml/min* | 1.0 |
| $C_0$ - adsorbate concentration at the column inlet | *mg/ml* | 0.1 |
| $q_m$ - maximum adsorption capacity | *mg/ml* | 14 |
| $k_d$ - dissociation rate constant | *mg/ml* | 0.025 |
| $k_1$ - adsorption rate constant | *ml/mg.min* | 0.20 |

The values of $k_1$, $k_d$ and $q_m$ shown in Table 1 were obtained by Chase (1984) using a batch experiment with the Langmuir isotherm.

The present work was originally intended to provide estimates for the parameters $k_d$ and $q_m$ in the Langmuir adsorption isotherm, given by Eq. (7), using the Particle Collision Algorithm (PCA). In a sensitivity analysis investigation it has been observed that the sensitivity coefficients for the parameter $k_d$ were too low. That fact led us to

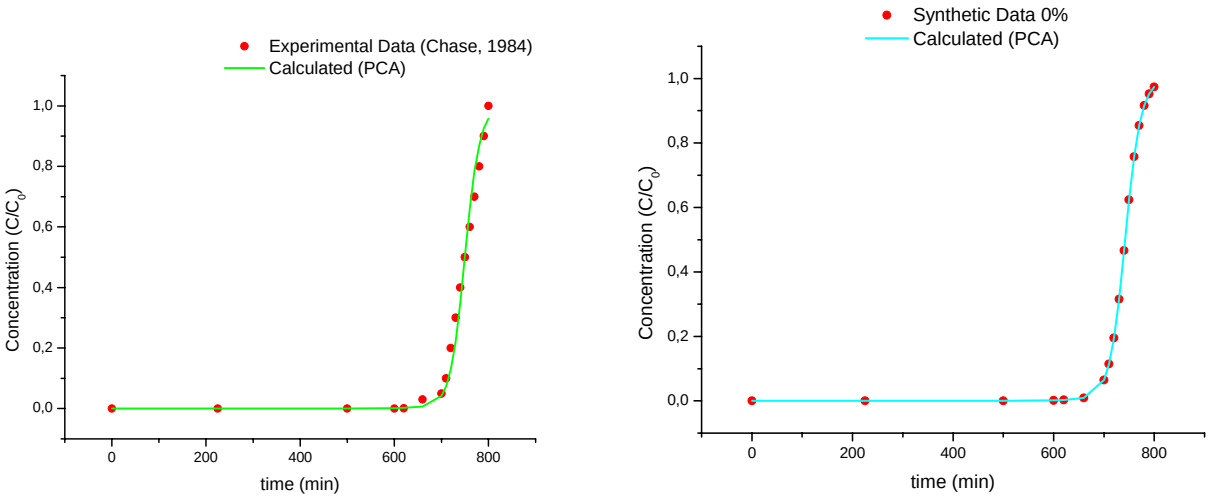
formulate the inverse problem to estimate only the parameter $q_m$, and the parameter $k_d$ for the specific substance we were looking at (lisozyme) was fixed in all cases at the value $0.025\,mg/ml$.

In Table 2 are shown the results obtained using experimental data (Chase, 1984) as well as synthetic data with 0%, 1%, 3%, 5% and 8% error. In the third column are shown the estimates obtained with PCA and in the last column is shown the value of the cost function. (Eq. (9)).

Table 2 – Estimates for the value of $q_m$, for lisozyme, using the PCA method, the experimental data obtained by Chase (1984) and synthetic data. $q_{m_{exact}} = 14.0\ mg/ml$

| Case | Data used | $\bar{q}_{m_{PCA}}\ mg/ml$ | $\bar{Q}(\vec{Z})$ |
|---|---|---|---|
| 1 | Chase (1984) | 14.20 | 3.3E-02 |
| 2 | 0% | 14.00 | 2.5E-09 |
| 3 | 1% | 13.98 | 1.7E-04 |
| 4 | 3% | 13.98 | 6.8E-04 |
| 5 | 5% | 13.99 | 3.0E-03 |
| 6 | 8% | 13.98 | 1.2E-02 |

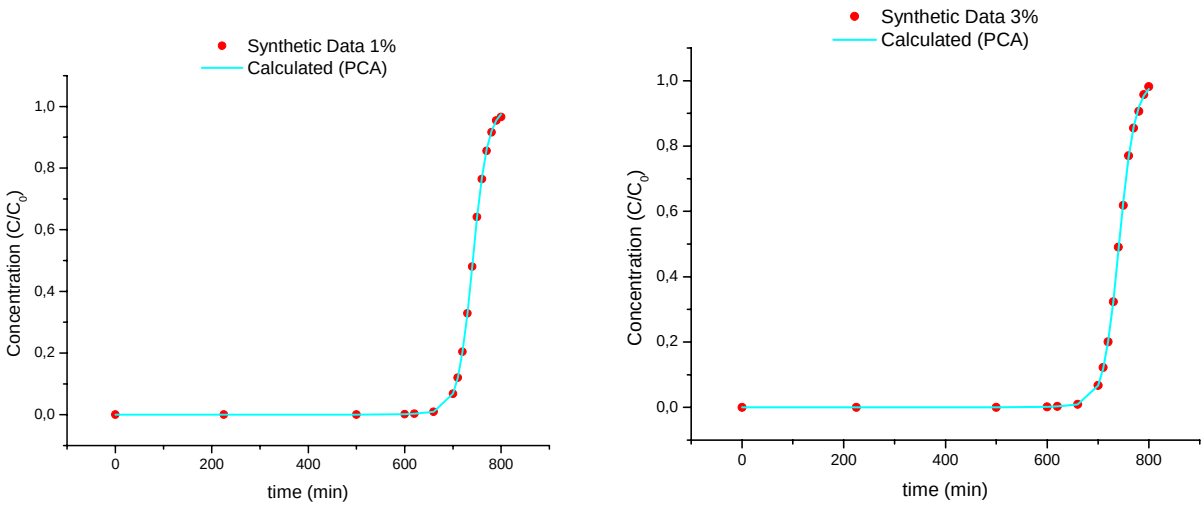
In Figs. 3-5 are shown the experimental data and the breakthrough curves calculated using the estimated values for the parameter $q_m$ given in Table 2.




(a) (b)

Figure 3 – Breakthrough curves for lisozyme using Thomas Model and PCA method.

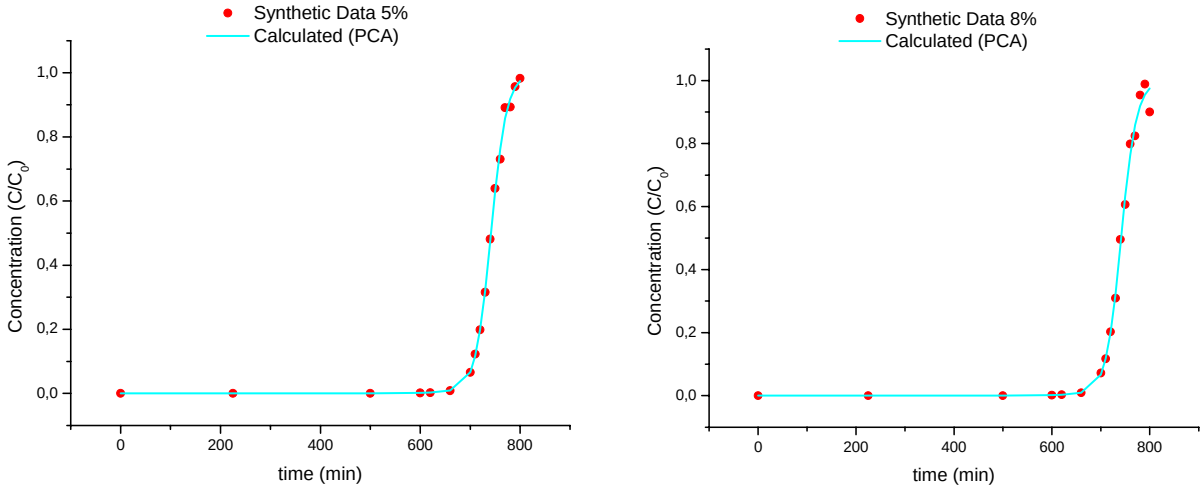
(a) Test-Case 1 with Experimental data (Chase, 1984). (b) Test-Case 2 with 0 % noise.




(a) (b)

Figure 4 – Breakthrough curves for lisozyme using Thomas Model and PCA method.

(a) Test-Case 3 with 1 % noise. (b) Test-Case 4 with 3 % noise.




(a) (b)

Figure 5 – Breakthrough curves for lisozyme using Thomas Model and PCA method.

(a) Test-Case 5 with 5 % noise. (b) Test-Case 6 with 8 % noise.

The results presented in Table 2 and Figs. 3-5 show an excellent agreement between the calculated breakthrough curves and the experimental data.

## 6. CONCLUSIONS

In the present work the Particle Collision Algorithm, using the Thomas model in the direct problem formulation, was able to yield good estimates for the parameter $q_m$ in all cases considered, using real and synthetic experimental data.

As the direct problem solution is analytical, and very fast to compute, the approach described in the present work for the solution of the inverse mass transfer problem is not computationally intensive, and therefore CPU time requirement is not an issue.

In future works other variations of PCA may be used in order to test its feasibility to solve this problem.

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## 7. REFERENCES

Ahmad, T. and Guiochon, G., 2007, "Numerical Determination of the Adsorption Isotherms of Tryptophan at Different Temperatures and Mobile Phase Compositions", Journal of Chromatography A, Vol. 1142, pp. 148-163.

Ahuja, S., 1991, "Chiral Separations: An Overview in Chiral Separations by Liquid Chromatography", J. Am. Chem. Soc., Vol. 113, pp. 1-26.

Blanch, H.W. and Clark, D.S., 1997, "Biochemical Engineering", Ed. Marcel Dekker, New York.

Câmara, L.T.D., Santana C.C. and Silva Neto, A.J., 2007, "Kinetic Modeling of Proteins Adsorption with a Methodology of Error Analysis", Journal of Separation Science. In press.

Chase, H.A., 1984, "Prediction of the Performance of Preparative Affinity Chromatography". Journal of Chromatography, Vol. 297, pp. 179-202.

Cuco, A.P.C., Silva Neto, A.J., Campos Velho, H.F. and Sousa, F.L., 2007, "Solution of an Inverse Adsorption Problem with an Epidemic Genetic Algorithm and the Generalized Extremal Optimization Algorithm", Proc. Inverse Problems, Design and Optimization Symposium, Miami, USA.

Duderstadt, J.J. and Hamilton, L.J., 1976, "Nuclear Reactor Analysis", John Wiley & Sons, New York.

Duderstadt, J.J. and Martin, W.R., 1979, "Transport Theory", John Wiley & Sons, New York.

Fellinger, A., Cavazzini, A. and Guichon, G., 2003, "Numerical Determination of the Competitive Isotherm of Enantiometers", Journal of Chromatography A, Vol. 986, pp. 207-225.

Folly, F.M., Silva Neto, A.J. and Santana, C.C., 2005, "An Inverse Mass Transfer Problem for the Characterization of Simulated Moving Beds Adsorption Columns", Proc. 5th International Conference on Inverse Problems Engineering: Theory and Practice, Cambridge, UK.

Forssén, P., Arnell, R. and Fornstedt, T., 2006, "An Improved Algorithm for Solving Inverse Problems in Liquid Chromatography", Computers and Chemical Engineering, Vol. 30, pp. 1381-1391.

Gritti, F. and Guichon, G., 2004, "Effect of the Ionic Strength of the Solution and the Nature of its Ions on the Adsorption Mechanisms of Ionic Species in RPLC – III. Equilibrium Isotherms and Overload Band Profiles on Kromasil – $C_{18}$", Journal of Chromatography A, Vol. 1047, pp. 33-48.

Guichon, G., 2002, "Preparative Liquid Chromatography (Review)", Journal of Chromatography, Vol. 965, pp. 129-161.

Guiochon, G. and Lin, B., 2003, "Modeling for Preparative Chromatography", Academic Press, Great Britain.

Kirkpatrick, S., Gellat Jr., C.D. and Vecchi, M.P., 1983, "Optimizing by Simulated Annealing", Science, Vol. 220, pp. 671-680.

Lage, L.F., Cuco, A.P.C., Folly, F.M., Soeiro, F.J.C.P. and Silva Neto, A.J., 2006, "Stochastic and Hybrid Methods for the Solution of an Inverse Mass Transfer Problem", Proc. III European Conference on Computational Mechanics, Lisboa, Portugal.

Lage, L.F., Cuco, A.P.C., Silva Neto, A.J., Folly, F.M. and Soeiro, F.J.C.P., 2006a, "Solution of an Inverse Mass Transfer Problem with a Hybridization of Artificial Neural Networks and Levenberg-Marquardt Method", Proc. 11th Brazilian Congress of Thermal Sciences and Engineering, Curitiba, Brazil.

Lugon Jr., J., Silva Neto, A.J. and Santana, C.C., 2007, "A Hybrid Approach with Artificial Neural Networks, Levenberg-Marquardt and Simulated Annealing Methods for the Solution of Gas-Liquid Adsorption Inverse Problems", Proc. Inverse Problems, Design and Optimization Symposium, Miami, USA.

Metropolis, N., Rosenbluth, A.W., Rosenbluth, M.N., Teller, H.A. and Teller, E., 1953, "Equation of State Calculation by Fast Computing Machines", Journal of Chemical Physics, Vol. 21, pp. 1087-1092.

Rice, G. R. and Do, D. D., 1994, "Applied Mathematics and Modeling for Chemical Engineers", Ed. John Wiley & Sons, New York.

Sacco, W.F., Oliveira, C.R.E. and Pereira, C.M.N.A., 2006, "Two Stochastic Optimization Algorithms Applied to Nuclear Reactor Core Design", Progress in Nuclear Energy, Vol. 48, No. 6, pp. 525-539.

Seidel-Morgenstein, A., 2004, "Experimental Determination of Single Solute and Competitive Adsorption Isotherms", Journal of Chromatography A, Vol. 1037, pp. 255-272.

Thomas, H., 1944, "Heterogeneous Ion Exchange in Flowing System", J. Am. Chem. Soc., Vol. 66, pp. 1664-1668.

Tondeur, D., Yu, F., Bonnot, K. and Luo, L., 2006, "Modeling Spreading-Pressure-Dependent Binary Gas Coadsorption Equilibria Using Gravimetric Data", Journal of Colloid and Interface Science, Vol. 293, pp. 342-352.
Vasconcellos, J.F.V., Silva Neto, A.J. and Santana, C.C., 2003, "An Inverse Mass Transfer Problem in Solid-Liquid Adsorption Systems", Inverse Problems in Engineering, Vol. 11, No. 5, pp. 391-408.

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